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THREE COORDINATION IN METAL COMPLEXES

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CONTENTS

I. INTRODUCTION

In this account we have attempted to review recent developments in the chemistry of three-coordinate compounds. We have excluded from consideration the well-established chemistry of three-covalent elements such as boron and nitrogen and have concentrated our attention on three-coordinated compounds of those elements for which the coordination number three would be considered atypical, or at least not the most favored configuration.

Nevertheless, the range of compounds reviewed is surprisingly broad, covering mineral species and other thermally and chemically stable compounds on the one hand and transient species involved in catalytic reactions and unstable species obtained by low temperature matrix isolation on the other hand.

For convenience of presentation the material is divided roughly according to ligand type, under the headings of "soft ligands" and "hard ligands". However, this arbitrary classification has not been rigidly adhered to, especially where it is found that a complex contains both "hard" and "soft" ligands.

Problems have inevitably arisen in deciding on the coordination number for some compounds containing π-bonding ligands such as olefins. Again, we have adopted a flexible approach by including compounds having ambiguous coordination where it seemed relevant or illuminating to do so.

II. COMPLEXES OF "HARD" LIGANDS

In this section we are concerned with metals which have a preferred coordination number greater than three but are constrained to three coordination by special features (predominantly steric) of the ligands to which they are bonded. This excludes such well established molecules as BX_3, NX_3, PX_3 etc. from consideration.

An obvious method to achieve abnormally low coordination is to use ligands which are so bulky as to preclude by steric hindrance either the attachment of further ligands or the attainment of a higher coordination by ligand bridging. Indeed, this technique had been adopted 25 years ago by Bradley, Mehrotra and Wardlaw [1] who succeeded in controlling the degree of polymerization of the metal alkoxides $[M(OR)_x]_n$ by using the steric effect of branched chain alkoxo groups. By using a tertiary alkoxo group a monomeric $Fe(OR)_3$ species was obtained [2] but the structure was not determined. In fact, the alkoxo group has considerable limitations, sterically speaking, because chain branching can only be effected on the carbinol carbon atom and not on the oxygen atom. In an ether, R_2O, the oxygen is uncharged and does not compete successfully as a ligand when other anionic ligands are present.

Nitrogen and carbon donor ligands have the advantage over oxygen in being present in anionic ligands such as dialkylamido R_2N^- and trialkyl methanido R_3C^-, which are capable of considerable steric hindrance. If the ligand is made excessively bulky there may be synthetic problems in producing a low coordination complex; in some cases it has been found expeditious to have supplementary neutral ligands available to stabilize the complex. In general terms we shall consider three-coordinate metal complexes of the types: (a) ML_3, (b) ML_2L' and (c) MLL'_2 (where L = a uninegative anionic ligand and L′ = a neutral ligand). The anionic ligands L will be confined to N-donors or C-donors but L′ may involve hard (THF) or soft (PR_3) donor atoms.

(a) Compounds of the type ML_3

The great majority of the compounds of this type involve the bis-trimethyl-silylamido group $(Me_3Si)_2N^-$ which was pioneered by Bürger and Wannagat [3] and later exploited by Bradley and co-workers [4] who had earlier obtained $Cr(NPr^i_2)_3$ with the diisopropylamido group. Recently, Lappert and co-workers [5] have extended this field to metal—carbon compounds by using the carbanion $(Me_3Si)_2CH^-$, which is isoelectronic with $(Me_3Si)_2N^-$.

(i) $M[N(SiMe_3)_2]_3$ compounds

Several of these compounds were synthesized using the reaction of the metal trichloride in THF solution with the sodio- or lithio-derivative of hexamethyldisilazane, e.g. eqns. (1) and (2).

$$(Me_3Si)_2NH + LiBu \rightarrow (Me_3Si)_2NLi + C_4H_{10} \quad (1)$$

$$MCl_3 + 3LiN(SiMe_3)_2 \rightarrow M[N(SiMe_3)_2]_3 + 3LiCl \quad (2)$$

In the cases of the titanium and vanadium compounds the above method required the modification of using the five-coordinate trimethylamine complexes $MCl_3(NMe_3)_2$ [6]. However, with scandium [7] and the lanthanides [8] the lithium silylamide—metal trichloride method was successful. The tris-derivatives ML_3 (M = Mn, Co and Ni) have not yet been isolated and it may be significant that these metals form three-coordinate silylamide complexes in lower valence states augmented by supplementary neutral ligands (see later sections).

Some physical properties of the ML_3 compounds are listed in Table 1. They are all crystalline solids which are reactive to water vapor and some are very oxygen-sensitive. Larger ligands such as THF do not coordinate, presumably due to steric hindrance. However, triphenylphosphine oxide forms 1 : 1 complexes with ML_3 (M = La, Eu and Lu; and presumably all of the other lanthanides) involving four-coordinate lanthanides [9]. The tris-silylamides react with alcohols to form metal alkoxides and $(Me_3Si)_2NH$. Some of the ML_3 compounds are thermally unstable and do not give reliable melting points or volatilities, but all are sufficiently stable and volatile to give mass spectra

TABLE 1

Physical properties of the tris(dimethylsilylamide) complexes

M in $M[N(SiMe_3)_2]_3$	Color	M.p. (°C)	Volatility [a]	N.m.r. (τ) [b]	Magnetic props. (μ_{eff} in B.M.)	Ref.
Sc	White	173	—	9.67	diamagnetic	7
Ti	Bright blue	dec.	dec.	—	1.62 [c]	7
V	Brown	—	95	—	paramagnetic [d]	7
Cr	Bright green	—	80	—	3.72 [e]	7
Mn	—	—	—	—	—	—
Fe	Dark green	—	80	—	5.94 [f]	7
Y	White	182	102	9.72	diamagnetic	10
La	White	147	101	9.75	diamagnetic	10
Ce	Yellow-brown	—	97	13.10	paramagnetic	10
Pr	Pale green	156	89	18.64	paramagnetic	10
Nd	Pale blue	162	87	15.60	paramagnetic	10
Pm	—	—	—	—	—	—
Sm	Pale yellow	156	84	11.58	paramagnetic	10
Eu	Orange	160	83	3.57	paramagnetic	10
Gd	White	161	82	—	7.82 [g]	10
Tb	—	—	—	—	—	—
Dy	—	—	—	—	—	—
Ho	Cream	162	83	—	—	10
Er	—	—	—	—	—	—
Tm	—	—	—	—	—	—
Yb	Lemon-yellow	163	80	—	—	10
Lu	White	168	78	9.70	diamagnetic	10

[a] Sublimation temp. (°C) at 10^{-2}—10^{-4} mm Hg; [b] Proton chemical shift in p.p.m. (T.M.S. = 10.00) in C_6D_6 soln.; [c] $g_{\parallel} = 1.993, g_{\perp} = 1.869$; [d] Room temp. value $\mu_{eff} \sim 2.38$; [e] $g_{\parallel} \sim 2, g_{\perp} \sim 4$; [f] $g_{\parallel} = 2.007, g_{\perp} = 6.021$; [g] $g_{\parallel} \sim 2, g_{\perp} \sim 8$.

TABLE 2

Comparison of molecular geometry parameters for $M[N(SiMe_3)_2]_3$, compounds, M = Ti, V, Cr, Fe (ref. 12,13)

	Ti	V	Cr	Fe
Metal—nitrogen bond length found (A)	1.929(4)	1.910(5)	1.903(6)	1.917(4)
"Expected" M—N length (i.e. Σ covalent radii) (A) *	1.981	1.948	1.935	1.967
Shortening of M—N length (A)	0.05	0.04	0.03	0.05
N—Si length (A)	1.750(3)	1.744(4)	1.740(4)	1.731(3)
Si—N—Si angle (°)	119.7(2)	121.0(2)	122.0(2)	121.2(2)

* Computed using radii calculated from bond lengths in the equatorial sites of trigonal-bipyramidal M(III) complexes.

containing the parent molecular ion ML_3^+ [10,11]. Molecular weights in cyclohexane (M = Cr and Fe) [7] and benzene (M = La, Sm and Eu) [10] showed that these compounds were monomeric in solution and X-ray single crystal analyses have proved that they are authentic three-coordinate compounds in the crystalline state [12,16]. They fall into two structural types: type (a) M = Ti, V, Cr, Fe, Al, Ga and In, have a trigonal planar MN_3 configuration (Table 2); type (b) M = Sc, Eu and Yb, have a pyramidal MN_3 configuration (Table 3).

NMR measurements showed that the colorless, diamagnetic compounds (M = Sc, Y, La and Lu) gave chemical shifts slightly down-field from TMS with a definite trend in the sense that the smaller the metal ion the greater was the shift. This could be a function of increasing covalency in the M—N bonds. The paramagnetic transition metal complexes gave no NMR signals although some (M = Ti, Cr and Fe) gave EPR signals, whereas the paramagnetic lanthanide compounds gave large pseudo-contact shifts [10].

Bürger et al. [17] measured the infrared and Raman spectra of the non-

TABLE 3

Some molecular geometry parameters for $M[N(SiMe_3)_2]_3$, compounds, M = Sc, Eu, Yb (ref. 16)

	Sc	Eu	Yb
M—N (A)	2.047(6)	2.259(9)	2.158(13)
N—Si (A)	1.751(2)	1.702(3)	1.720(4)
Si—N—Si (°)	121.6(4)	126.0(6)	122.1(8)

transition metal compounds (M = Al, Ga and In) and carried out a normal coordinate analysis with appropriate assignments of bands and calculations of force constants. The colored transition metal compounds (M = Ti, V, Cr and Fe) did not give Raman spectra but their infrared spectra were very similar to those of GaL_3 and they all showed a strong band at ~380 cm^{-1} due mainly to MN_3 antisymmetric stretching vibrations [7]. The intense band at ~900 cm^{-1}, assigned to the antisymmetric NSi_2 vibration, varied very little from Ti—Fe but it was much higher (950 cm^{-1}) for scandium. This is not surprising in view of the different crystal structure of ScL_3; in retrospect, it is significant that the scandium compound gave the strongest "extra" band around 420 cm^{-1}. This band was provisionally assigned as the symmetric MN_3 stretch and should be infrared inactive for a trigonal-planar MN_3 configuration. However, for the pyramidal MN_3 configuration there should be two infrared-active stretching vibrations and it is noteworthy that the 420 cm^{-1} band was weak for Ti, Cr and Fe, and absent for the V compound. The high value for ν_{as} NSi_2 for scandium suggests that there is minimal N → Sc p_π—d_π bonding in this compound. Infrared (and in several cases Raman) spectra were obtained for the lanthanide compounds [9]. A striking feature of the infrared spectra was the splitting of the MN_3 stretching vibration into a doublet at ~385 and 370 cm^{-1}, thus giving the two bands required for the pyramidal MN_3 configuration. The Raman spectra gave one coincident strong frequency (~387 cm^{-1}) but only a weak peak at the lower frequency. The infrared and, to a lesser extent, the Raman spectra lend support to the X-ray analysis [16], which shows that the lanthanide compounds have the pyramidal MN_3 configuration in the crystal lattice. A dipole moment measurement in benzene suggested that the structure relaxes to trigonal planar MN_3 (zero dipole moment) in solution; this was confirmed by infrared spectral measurements in solution, where the characteristic doublet at 385 and 370 cm^{-1} collapsed into one band [9]. The characteristic ligand vibration $\nu_{as}MNSi_2$, which showed only a small variation (around 900 cm^{-1}) along the series Ti, V, Cr and Fe, gave a marked trend in the lanthanides with a steady decrease from La to Lu. This trend could be correlated with M^{3+} radius since the value for Yb was precisely that predicted from its position as a pseudo-lanthanide according to its ionic radius.

The electronic absorption spectra were measured in cyclohexane solution for ScL_3 and the isostructural series ML_3 (M = Ti, V, Cr and Fe); provisional assignments were made as shown in Table 4 [18]. It is noteworthy that the band at 31.2 kK in ScL_3, which could not be a *d—d* transition and hence must be either charge—transfer or ligand—ligand in nature, had a molar extinction coefficient (ca. 500) comparable with those for bands in FeL_3 attributed to *d—d* transitions which must be spin-forbidden. This would suggest that the transition metal compounds are significantly covalent in character and require a molecular orbital treatment. Nevertheless, it was possible to interpret the proposed *d—d* transitions in terms of simple crystal field theory for M^{3+} ions in D_{3h} symmetry. Two crystal field splitting parameters *Ds* and *Dt*

TABLE 4

Spectral parameters for some of the bis (trimethylsilylamide) complexes

M in $M[N(SiMe_3)_2]_3$	Ground state [a]	d—d transitions [b]	Other transitions [c]	Ds [d]	Dt [d]	CFSE [e]
Ti	$^2A_1'$	4.8(10); $^2A_1' \rightarrow {}^2E''$ 17.4(122); $^2A_1' \rightarrow {}^2E'$	28.6(500)	−4.286	−0.051	8900
V	$^3E''$	12.0(60); $^3E'' \rightarrow {}^3E'$ 15.9(150); $^3E'' \rightarrow ({}^3A_1'', {}^3A_2'')$ 19.2(268); $^3E'' \rightarrow {}^3E''$	24.7(480) 28.1(450)	−5.600	0.100	16 600
Cr	$^4A_2'$	11.8(100); $^4A_2' \rightarrow ({}^4A_1'', {}^4A_2'')$ 14.8(550); $^4A_2' \rightarrow {}^4E$	25.3(3700) 31.4(3700) 33.6(2800)	−7.045	0.404	29 000
Fe	$^6A_1'$	16.1(400); $^6A_1' \rightarrow ({}^4A_1'', {}^4A_2'')$ 20.0(450); $^6A_1' \rightarrow {}^4E$	25.3(1500) 29.7(1500)	−5.800	0.770	0

[a] Data taken from ref. 18.

[b] Band maxima in kK; molar extinction coefficients (ϵ_M) in parentheses.

[c] Band maxima and ϵ_M as in [b]; probably charge-transfer or ligand—ligand transition.

[d] Racah parameters used were: V^{3+}, $B = 860$ cm^{-1}; Cr^{3+}, $B = 1030$ cm^{-1}; Fe^{3+}, $B = 1030$; $C = 3850$ cm^{-1}.

[e] Crystal Field Stabilization Energy in cm^{-1}.

are required; the energies of the one-electron d-orbitals are then given as follows

$d_{z^2}(a'_1) = 2Ds + 6Dt$

$d_{xz}, d_{yz}(e'') = Ds - 4Dt$

$d_{x^2-y^2}, d_{xy}(e') = -2Ds + Dt$

The values of Ds and Dt for the ground state electronic configuration for each ion are given in Table 4 together with the calculated crystal field stabilization energy (CFSE).

For the MN_3 unit with D_{3h} symmetry let us define the 3-fold axis along the z-direction; the crystal field stabilizes the d_{z^2} and d_{xz}, d_{yz} orbitals relative to the d_{xy}, d_{xy}, $d_{x^2-y^2}$ orbitals. In terms of covalent bonding the d_{xy}, $d_{x^2-y^2}$ orbitals become predominantly σ-anti-bonding orbitals due to overlap in the x,y plane with the ligand orbitals. In the cases of Ti^{3+}, V^{3+} and Cr^{3+}, the d_{z^2} orbital was lowest in energy, but the next level (d_{xz}, d_{yz}) becomes steadily lower in energy with increasing atomic number to the point when it becomes lower than d_{z^2} in Fe^{3+}. In considering the possibility of covalent bonding it is reasonable to expect a small degree of σ-bonding involving the d_{z^2} orbital and ligand orbitals but not for the d_{xz}, d_{yz} orbitals; thus, the latter should be lower in energy than d_{z^2}, as found in FeL_3. To explain the anomalous order for ML_3 (M = Ti, V and Cr) it is necessary to propose that the d_{xz} and d_{yz} orbitals are involved in ligand → metal π-bonding thereby being raised in energy relative to d_{z^2}. If the degree of π-bonding decreases in the above order then the pattern of one-electron d-orbital energies can be explained. However, this is a very naive treatment because π-bonding should be considered in terms of the molecular symmetry D_3, since the ligand framework makes a dihedral angle (ca. 50°) with the MN_3 plane [12] and the system is very complicated. This suggestion of some π-bonding receives support from the comparison of bond lengths. Returning to a simple crystal field model we note the steady increase in CFSE in the order $Cr > V > Ti$ and that in all cases it is substantial and comparable with the stabilization caused by six ligands in an octahedral complex. Since the iron compound is a d^5 high spin case there is no stabilization energy, although there is considerable splitting of the energy levels ($\sim$21 000 cm^{-1} between d_{xz}, d_{yz} and $d_{x^2-y^2}$, d_{xy} levels). It is unfortunate that MnL_3 has not yet been isolated and there seems no particular reason why it should not exist. In fact, it would be expected to have ca. 8 000 cm^{-1} of CFSE assuming that it would be high spin as in FeL_3. The crystal field diagram for FeL_3 shows that the strength of the crystal field splitting with this ligand is only about one half of the value required to cause spin pairing to the $^2A'_1$ ground state and this is consistent with variable temperature magnetic susceptibility and Mössbauer spectra measurements.

For the d^1, d^3 and d^5 species (Ti, Cr and Fe) a detailed study of magnetic susceptibilities [18] and EPR [19] was carried out over the temperature range 98—298 K. The vanadium compound gave no EPR signals ($^3E''$ ground state with a low lying $^3A'_2$ excited state) and difficulties were experienced in measuring magnetic susceptibilities, but it was shown to be paramagnetic at room temperature ($\mu_{eff} \sim 2.4$ B.M.).

For the titanium compound, after correcting for diamagnetism and for a significant contribution from the second-order Zeeman effect ($217 \cdot 10^{-6}$ c.g.s. units due to the $^2E''$ excited state at 4 800 cm^{-1} above the ground state), the paramagnetism fitted the Curie Law over the entire temperature range with $\mu_{eff} = 1.62 \pm 0.04$ B.M. This is in excellent agreement with the value of 1.65 B.M. that was deduced from the EPR signal ($g_0 = 1.911$) obtained from the isotropic solution. The EPR spectrum of a frozen (133 K) toluene solution of TiL_3 showed the anisotropy expected for an axially symmetric species ($g_\parallel = 1.993$; $g_\perp = 1.869$). Moreover, the fact that $g_\perp < g_\parallel \sim 2$ confirmed the $^2A'_1$ (d_{z^2}) ground state since theory required in this case: $g_\perp = 2\,(1—3\zeta/\Delta)$, where ζ = the spin—orbit coupling parameter and Δ is the excitation energy for $^2A'_1 \rightarrow {}^2E''$. Using the free-ion value for ζ (154 cm^{-1}) with $\Delta = 4\,800$ cm^{-1}(from the electronic spectrum) required $g_\perp = 1.808$, which is somewhat low, whereas the observed value of $g_\perp = 1.869$ would be calculated using $\zeta = 108$ cm^{-1}, which is 70% of the free-ion value. Such behavior is usually interpreted as due to covalent bonding of the metal ion. It is noteworthy that the very weak band at 4 800 cm^{-1} (symmetry forbidden transition; $^2A'_1 \rightarrow {}^2E''$), which was detected with difficulty, plays an important role in determining the values of μ_{eff}', $g_\parallel$ and $g_\perp$. The bright blue color of the compound is caused by the stronger (symmetry allowed $^2A_1' \rightarrow {}^2E'$) band at 17 400 cm^{-1}.

The chromium compound (d^3) obeyed the Curie—Weiss law ($\theta = —4°$) with $\mu_{eff} = 3.73 \pm 0.02$ B.M. over the range 123—298 K, as expected for the ground state $^4A'_1$. No EPR signal was observed for a solution in toluene but the polycrystalline solid gave signals showing anisotropy with “effective” g-values of $g_\parallel \sim 2$ and $g_\perp \sim 4$. This was shown to be due to a substantial zero-field splitting of the Kramers doublets arising from mixing of excited states with the $^4A'_1$ ground state. Solution of the appropriate spin Hamiltonian gave $D = 1.85 \pm 0.05$ cm^{-1} while variable temperature intensity measurements at low (near liquid He) temperatures proved that D is negative. This means that the $M_s = \pm 3/2$ Kramers doublet is at lower energy than $M_s = \pm 1/2$ (they are separated by $2D$ in energy). From the crystal field treatment of the electronic spectrum the data were available to calculate D using second-order perturbation theory. The calculated value of —2.3 cm^{-1} was in remarkably good agreement with the experimentally determined value of —1.85 cm^{-1} bearing in mind that the free-ion value for ζ (273 cm^{-1}) was used in terms involving $(\zeta)^2$. A reduction of ζ to 90% of the free-ion value would give agreement.

More detailed studies were carried out on the d^5 system FeL_3. The compound obeyed the Curie—Weiss law ($\theta = —10°$) with $\mu_{eff} = 5.93 \pm 0.01$ B.M. over the range 98—298 K. A toluene solution gave no EPR signal but the polycrystalline solid showed g-value anisotropy with "effective" $g_{\parallel} \sim 2, g_{\perp} \sim 6$, corresponding to a zero-field splitting of the $^6A'_1$ ground state. Solution of the spin Hamiltonian gave $D = 1.00 \text{ cm}^{-1}$ and depopulation experiments showed the sign of D to be negative so that the $M_s = \pm 5/2$ Kramers doublet lies lowest in energy. Approximate calculations from the crystal field diagram gave $D = -0.4 \text{ cm}^{-1}$, which is at least of the correct sign and within an order of magnitude of the numerical value. Some oriented single crystal EPR measurements were carried out and gave exact agreement with the equation $g_\theta^2 = g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta$, where g_θ is the g-value when the needle axis of the crystal is at the angle θ to the magnetic field direction.

The iron compound also gave rather interesting Mössbauer spectra [20]. At 77 K a remarkably large quadrupole splitting ($1/2\, e^2Qq = +5.12 \text{ mm sec}^{-1}$) and a small isomer shift ($\delta = 0.30 \text{ mm sec}^{-1}$) were observed. The large quadrupole shift was attributed to the charge distribution (xy plane) in this covalent molecule. Cooling to 4.2 K produced a magnetic hyperfine spectrum of five broad lines which was resolved into the expected six lines on applying a small magnetic field. At 1.4 K a six-line spectrum was obtained, even at zero field. This behavior is consistent with the $M_s \pm 5/2$ Kramers doublet lying lowest and being preferentially populated at 1.4 K since a long relaxation time would result due to the transition $M_s + 5/2 \leftrightarrow -5/2$ being forbidden ($\Delta M_s = \pm 1$). The long relaxation time sustains a sharp hyperfine spectrum at 1.4 K but on raising the temperature to 4.2 K the $M_s = \pm 3/2$ level (at $4D \text{ cm}^{-1}$ higher energy) becomes populated, broadens the lines, and reduces the effective field at the nucleus. From the line shape variation with temperature it was also deduced that the sign of the electric field gradient q is positive and that the fluctuating effective magnetic field of the nucleus is along the z axis ($+z \leftrightarrow -z$). The hyperfine field was 175 kG at 1.5 K and 155 kG at 4.2 K, consistent with $D/k \sim -1$ K and clearly ruling out a spherically symmetrical ^6S state, for which $q = 0$ and the hyperfine field would be $\sim 550 \pm 50$ kG. Thus, the crystal field interpretation of the electronic spectrum, magnetic susceptibility, EPR spectrum and Mössbauer spectrum, gives a consistent picture of FeL_3 with a $^6A'_1$, ground state, considerable zero-field splitting, and significant covalent bonding in the xy plane.

Preliminary results on the photoelectron spectra of ML_3 compounds suggest that the highest filled molecular orbitals may contain essentially nitrogen lone pairs rather than d electrons [21].

Some preliminary spectroscopic work has been carried out on the three-coordinated lanthanide compounds LnL_3. Although crystal field effects normally play only a minor role in the electronic spectra of lanthanide ions, the very considerable effect produced by the trigonal array of silylamide ligands on the transition metal ions gave expectations that perturbations of $4f$-electron levels might be revealed in the spectra of LnL_3. Comparison of the spectra of pentane solutions of LnL_3 (Ln = Pr and Nd) with the spectra of the corresponding aquo-ions in water showed significant changes [10]. In PrL_3 the transitions $^3H_4 \rightarrow {}^3P_{2,1,0}$ are clearly split due to the trigonal crystal field splitting of the $^3P_2$ and $^3P_1$ levels. The overall splitting of $^3P_2$ is approximately 1200 cm^{-1}. Considerable splitting also occurs in the spectrum of NdL_3. The nephelauxetic parameter β = (σcomplex/σaquo-ion, where σ = energy of a specific transition) [23] was calculated for PrL_3 (β = 0.993) and NdL_3 (β = 0.978). This parameter is usually considered to indicate the reduction of inter-*f*-orbital electron repulsions due to increased shielding caused by σ-donation, with σ-donation being roughly inversely proportional to β. The above results suggest that the Ln—L bonds do involve a significant covalent contribution, which would be expected to increase with decrease in Ln^{3+} radius as suggested by the infrared and NMR spectral data discussed earlier. The colors of LnL_3 compounds also call for comment. All of them show strong absorption bands in the ultraviolet region (>25 000 cm^{-1}) which, at least partly, are due to ligand → metal charge-transfer transitions and/or ligand—ligand transitions. The metals (Eu, Yb and Sm) are known to be more easily reduced to the bivalent state, so one would expect the ligand → metal transition to be shifted to lower energy. Therefore, it is noteworthy that the orange colored EuL_3 gave a strong absorption beginning at ca. 16 000 cm^{-1} and that YbL_3 and SmL_3 are yellow solids.

We have already mentioned that LaL_3 and LuL_3 are diamagnetic, while the other LnL_3 compounds gave paramagnetic NMR shifts for the ligand protons. Some preliminary magnetic susceptibility and EPR studies have been carried out on GdL_3 [10]. The metal ion in this highly paramagnetic compound has seven unpaired electrons (Gd^{3+}, $^8S_{7/2}$) and susceptibility measurements at 98 K (μ_{eff} = 7.75 B.M.) and 298 K (μ_{eff} = 7.89 B.M.) suggest that it obeys the Curie law (theoretical μ_{eff} = 7.94 B.M.). The polycrystalline powder gave EPR signals at room temperature corresponding to the anisotropic *g*-values expected for an axially symmetric system. The "effective" *g*-values, $g_{\parallel} \sim 2$ and $g_{\perp} \sim 8$, further suggest that there is a substantial zero-field splitting of Gd^{3+} in this molecule (cf. Cr^{3+} and Fe^{3+}).

Single crystal X-ray diffraction studies have played a major role in the area of three-coordinate complexes of bulky amide ligands. The first of these compounds to be studied crystallographically was the iron compound $Fe[N(SiMe_3)_2]_3$ [12]. This was found to have precise D_3 symmetry with accurately planar FeN_3 and $FeNSi_2$ groups (see Fig. 1). Subsequently, molecular geometry parameters for the isostructural titanium, vanadium and chromium analogues were obtained [13]. Comparison of these results has allowed a detailed study to be made of the metal—nitrogen and silicon—nitrogen bond lengths, both of which are likely to be affected by ligand-to-metal π-bonding, with changes in *d*-orbital population. The results obtained from these crystallographic studies are summarized in Table 2. In this table, values for the "expected" M—N distance have been computed using radii calculated from bond lengths in the equatorial sites of trigonal-bipyramidal M(III) complexes. Consideration of these data shows that for Ti, V and Cr the M—N bonds seem to be slightly shorter than expected, that the shortening is greatest for titanium and that taken in conjunction with the small but

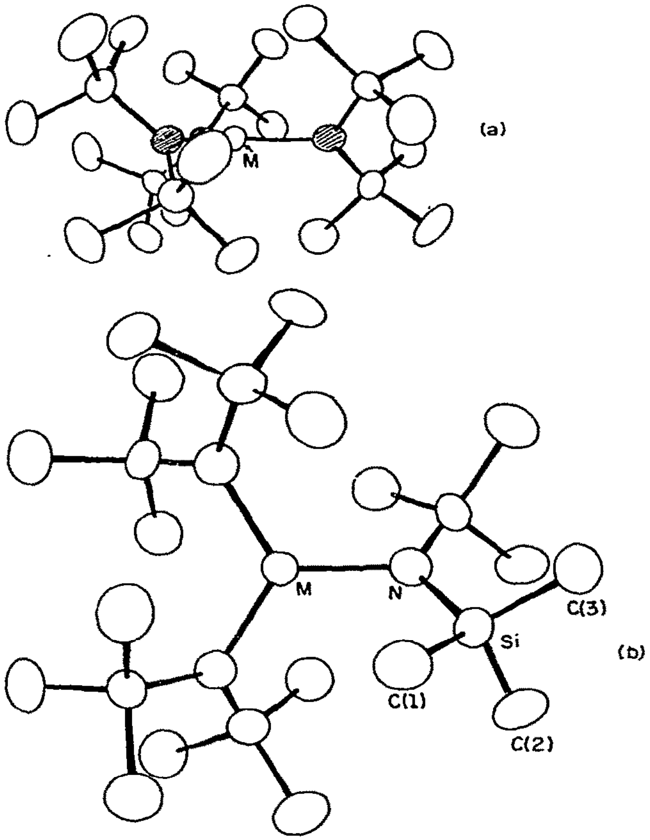
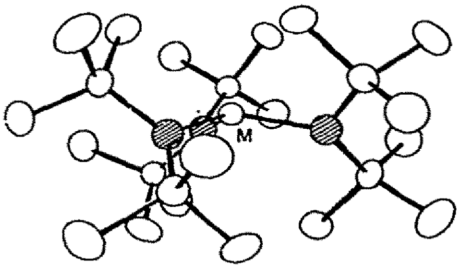


Fig. 1. Trigonal-planar compounds $M[N(SiMe_3)_2]_3$ (M = Ti, V, Cr, Fe, Al, Ga, In): (a) projection on to 001, and (b) view in a direction normal to the *c*-axis of the unit cell.

regular trend in the N—Si lengths there is some indication of a slight strengthening of the M—N bond at the expense of a slight weakening of the N—Si bond from Cr to Ti. However, the differences are small and in view of the many assumptions which have been made, it is unwise to draw any firm conclusions from these comparisons.

Further data on the tris-silylamides have been obtained by studies on the aluminum [14,22], indium [15] and gallium [22] derivatives. These are isostructural with the iron compound. The M—N distances are 1.84(1) (Al), 1.857(8) (Ga) and 2.057(12) Å (In), in each case very close to the values estimated for a normal σ-bond. This is rather surprising in the case of Al (which can be considered to be a d^0 species) and it is suggested [22] that the bulk of the silylamide ligand and the resulting intramolecular interligand repulsive interactions will not allow much shortening of this bond. The N—Si distances of 1.74—1.75 Å are at the longer end of the range found for the Ti—Fe series.

Although the compounds $M[N(SiMe_3)_2]_3$, M = Sc, Eu and Yb are appar-



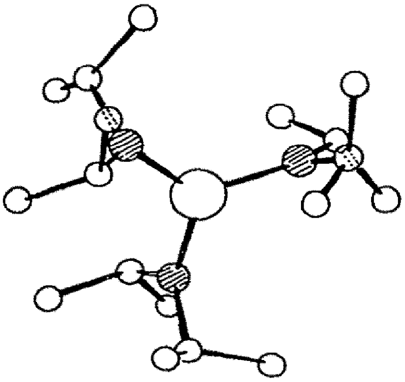


Fig. 2. Trigonal-pyramidal compounds $M[N(SiMe_3)_2]_3$ (M = Sc, Yb, Eu); in a direction normal to the *c*-axis.

Fig. 3. Tris(diisopropylamido)chromium(III).

ently isostructural with the iron compound, detailed crystallographic analysis [16] showed one significant difference between the molecular structures of these three compounds and the Ti—Fe series. In the crystal structures of the Sc, Eu, and Yb complexes, the three silylamide ligands adopt the same D_3 arrangement as in the structure of the iron complex; the metal ion, however, appears to be disordered, lying ~0.4 Å on either side of the N_3 plane. Figure 2 shows the structure of these molecules with only one metal site occupied. It has been suggested that this type of structure arises from two factors. One is that the metal—silylamide bonds contain a considerable degree of ionic character; thus, the positioning of the three ligands is not subject to rigid stereochemical requirements. The second is that the best arrangement of the three bulky ligands is one of D_3 symmetry with the ligands "pulled in" to their chosen positions by mutually attractive van der Waals forces. This in turn squeezes the metal ion out of the N_3 plane. The bond lengths and angles resulting from the choice of this model for the molecular structure are certainly sensible, as can be seen from Table 3. A particular feature of these parameters is the geometry of the N—Si group. The short N—Si distances and increasing Si—N—Si angles both support the idea of some negative charge being located on the ligand.

(ii) $M(NPr^i_2)_3$ compounds

Some mention should be made of tris-diisopropylamido compounds before leaving ML_3 compounds containing bulky amido ligands. Although $Cr(NPr^i_2)_3$ has been well characterized, there is a paucity of data on other species of this kind. Bradley and co-workers [7] have attempted the synthesis of $Ti(NPr^i_2)_3$ and $V(NPr^i_2)_3$ without success but Chien and Kruse [24] have reported EPR signals for $Ti(NPr^i_2)_3$ formed *in situ*. The yttrium compound $Y(NPr^i_2)_3$ (pale yellow crystals) and the ytterbium compound $Yb(NPr^i_2)_3$ (orange crystals) have been prepared; the neodymium compound was obtained as the THF complex $Nd(NPr^i_2)_3$ (THF) (light blue crystals) [9]. The latter is presumably a four-coordinate neodymium complex, and reveals a subtle difference between $Nd(NPr^i_2)_3$ and $Yb[N(SiMe_3)_2]_3$, since the latter does not form a stable complex with THF.

The chromium compound $Cr(NPr^i_2)_3$ has been the subject of detailed studies [4,25—29]. Its monomeric nature in solution [4] suggested that it involved three-coordinate chromium; this was subsequently confirmed by X-ray single crystal analysis [6], which showed a molecular symmetry approximating to D_3. The molecule lies in a general position in a triclinic unit cell, and the orientations of the isopropyl groups in the three ligands are quite different (see Fig. 3). Nevertheless, the CrN_3 and $CrNC_2$ groups are all quite planar (max. deviation of any atom from its plane is 0.014 Å). It would seem likely therefore that the planarity of the nitrogen atoms arises from the involvement of the lone pairs (assumed to have almost pure *p* character) in ligand-to-metal π-bonding. The short (1.84(1)—1.88(1) Å) Cr—N distances tend to support this idea.

Magnetic susceptibility measurements [25] confirmed that $Cr(NPr^i_2)_3$ behaved as a magnetically dilute species with a magnetic moment (μ_{eff} = 3.80 B.M.) which corresponds to three unpaired electrons (cf. $Cr[N(SiMe_3)_2]_3$). The pure compound does not give an isotropic EPR signal at room temperature, but a frozen solution (toluene, 130 K) gave *g*-value anisotropy ($g_\parallel$ = 2.0, $g_\perp$ = 4.0) corresponding to an axially symmetric species with a large zero-field splitting of the chromium ion [26]. This compound is extremely oxygen-sensitive and in solution it forms an unstable 1 : 1 complex with dioxygen (which has an intense EPR signal); thus, it may form a Cr(V) peroxo species such as $Cr(O_2)(NPr^i_2)_3$ [28]. Another very unstable (explosively so!) compound is obtained at lower temperature with the uptake of 1.5 mol O_2/mol $Cr(NPr^i_2)_3$ [29]. On the other hand, addition of nitric oxide gave a stable diamagnetic complex $Cr(NO)(NPr^i_2)_3$ [27]. This compound and $Cr(NO)[N(SiMe_3)_2]_3$, which is also stable, may be considered as a formally Cr(II), d^4 complex, with the NO group acting as a three-electron donor. In this pseudotetrahedral (C_{3v} local symmetry) complex the crystal field effect of the ligand in conjunction with strong π-acceptor behavior of NO^+ is sufficient to cause spin-pairing of the d^4 electrons in low energy *d*-orbitals to produce a diamagnetic compound. If the NPr^i_2 ligands act as π-donors in addition to the Cr—N σ-bonds, then the chromium can share in an 18-electron valency configuration. The chemical stability of this compound was demonstrated by ligand exchange in which the NPr^i_2 ligands could be displaced by OBu^t without loss of NO (e.g., eqns. 3 and 4).

$$Cr(NO)(NPr^i_2)_3 + 2Bu^tOH \rightarrow Cr(NO)(OBu^t)_2(NPr^i_2) + 2Pr^i_2NH \quad (3)$$

$$Cr(NO)(NPr^i_2)_3 + 3Bu^tOH \rightarrow Cr(NO)(OBu^t)_3 + 3Pr^i_2NH \quad (4)$$

Note that the tertiary butoxy group alone does not have the shielding power to produce the monomeric three-coordinate complex $Cr(OBu^t)_3$. Instead a very unstable dimer $Cr_2(OBu^t)_6$ is obtained which is readily oxidized to the stable monomer $Cr(OBu^t)_4$ (4). Therefore one NO group exerts a very impressive stabilizing effect.

(iii) $M[CH(SiMe_3)_2]_3$ compounds

To complete this section on ML_3 compounds we review some interesting compounds involving bulky ligands with carbon donor atoms, i.e. low coordination metal alkyls.

Bower and Tennent [30] isolated a remarkable series of ML_4 compounds (M = Ti, V, Cr, Mn, Fe, Co, Zr and Hf), using the 1-norbornyl (C_7H_{11}) ligand, which has tertiary carbon—metal bonding. A tris-derivative of chromium was obtained with the bulkier 2,2,3-trimethyl-1-norbornyl group.

Recently, Lappert et al. [5] used the bulky alkyl $(Me_3Si)_2CH^-$, which is isoelectronic with $(Me_3Si)_2N^-$, to obtain the tris-derivatives of yttrium, titanium, vanadium and chromium. The bright-green CrL_3 compound is monomeric in benzene and paramagnetic (μ_{eff} = 3.7 B.M.); it has an EPR spectrum (g values at ~2 and ~4) consistent with the presence of a d^3 ion having a large zero-field splitting. It will be extremely interesting to find how the crystal structure of this compound compares with that of $Cr[N(SiMe_3)_2]_3$ because the two ligands are isoelectronic but not isostructural since the methine proton on $(Me_3Si)_2CH^-$ takes the place of the lone pair on nitrogen in $(Me_3Si)_2N^-$. Clearly in $(Me_3Si)_2CH^-$ there will be no possibility of ligand → metal π-bonding in the conventional sense. The chromium compound reacted with nitric oxide and was presumed to have formed $Cr(NO)[CH(SiMe_3)_2]_3$ ($\nu_{NO} = 1672\ cm^{-1}$) by analogy with $Cr(NO)[N(SiMe_3)_2]_3$. With trityl chloride $Cr[CH(SiMe_3)_2]_3$ liberated $(C_6H_5)_3C$ radicals and appears to have formed the Cr(IV) compound $CrCl[CH(SiMe_3)_2]_3$. The white yttrium compound was diamagnetic (τ values 9.60, 10.53) and gave an infrared band at $402\ cm^{-1}$ ascribed to the M—C stretching vibration. Yttrium also forms the 1 : 2 complex with THF, thus differing from $Y[N(SiMe_3)_2]_3$, which does not combine with THF. Similarly, the scandium compound $Sc[CH(SiMe_3)_2]_3(THF)_2$ was isolated. The blue-green $Ti[CH(SiMe_3)_2]_3$ gave an EPR signal (g_0 = 1.968) and two infrared bands (432, 403 cm^{-1}) which were assigned to ν_{TiC3} although only one is required for a trigonal-planar TiC_3 unit. The blue-green $V[CH(SiMe_3)_2]_3$ similarly gave two bands (460 and 403 cm^{-1}), as did the chromium compound (449 and 403 cm^{-1}); this could indicate a pyramidal MC_3 structure.

(iv) ML_3 radicals

In a recent exciting development, Lappert and co-workers [31] have synthesized three-coordinate radicals of the Group IV elements (Si, Ge, Sn and Pb) using the bulky ligands $(Me_3Si)_2CH^-$ and $(Me_3Si)_2N^-$. The compounds of type ML_3, e.g., M = Si, Ge and Sn, with L = $(Me_3Si)_2CH^-$, and M = Ge and Sn, with L = $(Me_3Si)_2N^-$, were obtained by a photochemical synthesis coupled with reaction of LiL with either MCl_2 (M = Ge or Sn) or Si_2Cl_6 (eqns. 5—7).

$$MCl_2 + 2LiL \rightarrow ML_2 \xrightarrow{h\nu} ML_3 \quad (5)$$

$$Si_2Cl_6 + 6LiL \xrightarrow{h\nu} LSiCl_2 - SiCl_2L + L_2SiCl - SiCl_3 \quad (6)$$

$$L_2SiCl{-}SiCl_3 \rightarrow SiCl_4 + SiL_2 \rightarrow SiL_3 \quad (7)$$

The three-coordinate species were all characterized by their EPR spectra, and their stabilities in hexane at 30°C varied from ca. 10 min for $Si[CH(SiMe_3)_2]_3$ to 3 months for $Sn[N(SiMe_3)_2]_3$. The spectra showed nuclear hyperfine coupling to the central element and superhyperfine coupling to the methine proton in $(Me_3Si)_2CH^-$ or the nitrogen in $(Me_3Si)_2N^-$; the data are shown in Table 5. This work demonstrates the extraordinary power of the use of bulky ligands and opens up a field of considerable potential interest and scope.

(b) Compounds of the type ML_2L'

Some transition metals (Mn, Co and Ni) were found by Bürger and Wannagat [3] to give bivalent silylamides ML_2; to date no tervalent three-coordinate compounds of these metals of the kind ML_3 have been characterized. The nonexistence of NiL_3 is perhaps explicable in terms of the Effective Atomic Number rule (L as $4e^-$ donor), but the non-existence of MnL_3 seems odd indeed. However, in the course of studying these potentially two-coordinate ML_2 compounds some three-coordinate compounds of the type ML_2L', were isolated. Thus, in attempting to grow crystals of "$Mn[N(SiMe_3)_2]_2$" by sublimation [33], it was found that the compound had taken up one molecule of THF giving the crystalline three-coordinate Mn(II) high-spin (μ_{eff} = 5.91 B.M.) compound $Mn[N(SiMe_3)_2]_2(THF)$ [32]. Crystallographic analysis showed the structure to contain two independent molecules with very similar geometries. One molecule is shown in Fig. 4. The main features of the geometry are a

TABLE 5

ESR parameters for main-group ML_3 derivatives

Radical *	Solvent	g	a(H) **	a(N) **	a(M) **
$Si[CH(SiMe_3)_2]_3$	Benzene	2.0027	0.48	—	19.3(^{29}Si)
$Ge[CH(SiMe_3)_2]_3$	Benzene	2.0078	0.38	—	9.2(^{73}Ge)
$Sn[CH(SiMe_3)_2]_3$	Benzene	2.0094	0.21	—	169.8(^{117}Sn) 177.6(^{119}Sn)
$Ge[N(SiMe_3)_2]_3$	n-Hexane	1.9991	—	1.06	17.1(^{73}Ge)
$Sn[N(SiMe_3)_2]_3$	n-Hexane	1.9912	—	1.09	317.6(^{117}Sn) 342.6(^{119}Sn)

* Data from J.D. Cotton, C.S. Cundy, D.H. Harris, A. Hudson, M.F. Lappert and P.W. Lednor, Chem. Commun., (1974) 651.

** In mT.

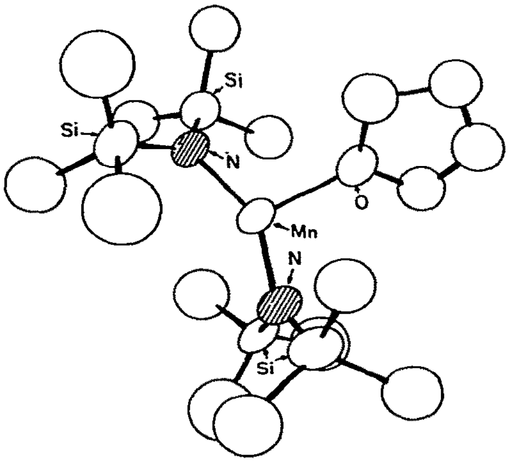


Fig. 4. $Mn[N(SiMe_3)_2]_2(THF)$, viewed almost normal to the MnN_2O plane.

planar MnN_2O unit with large N—M—N angles (145 and 150°) and small N—M—O angles (101—113°) — the variations probably arising from packing effects. The structure may be envisaged to arise from attachment of the THF ligand (followed by only a small rearrangement of the silylamide ligands) to a molecule of $Mn[N(SiMe_3)_2]_2$, which is believed to have a linear D_{2d} structure [33]. A discussion of the bonding is limited by a number of factors, one being the low accuracy of the molecular parameters and the artificial shortening of bond lengths arising from the high thermal motion of the molecules in the crystal (the melting point of the compound is only ~50°C). A second factor is the scarcity of suitable structural data for comparison. In spite of these complications, however, the Mn—O distance of 2.16(2) Å is in reasonable agreement with other Mn(II)—O bond lengths, whereas the Mn—N (average = 1.99(2) Å) is the shortest yet recorded. Some shortening might be expected if the metal—silylamide bonding parallels that in $Fe[N(SiMe_3)_2]_3$, since both metal atoms have d^5 configurations. On the other hand, the N—Si distances (average 1.69(2) Å) suggest not only little or no metal—nitrogen π-interaction, but even increased N → Si π-bonding. However, these distances are particularly susceptible to artificial shortening by thermal motion, and should not be regarded as very accurate. Clarification of the bonding in this compound must therefore await redetermination of the structure at a lower temperature and more comparable structure analyses.

It seems pertinent to observe that $Cr[N(SiMe_3)_2]_2$ takes up two molecules of THF forming a *trans* square-planar, high-spin complex [34]. Moreover, attempts to form $Fe[N(SiMe_3)_2]_2$ always seem to produce $Fe[N(SiMe_3)_2]_3$, even in THF solution and $Co[N(SiMe_3)_2]_2$, which coordinates with some neutral ligands, does not yield a stable crystalline complex with THF. There is evidence in the preparation of $Ni[N(SiMe_3)_2]_2$ that it occludes

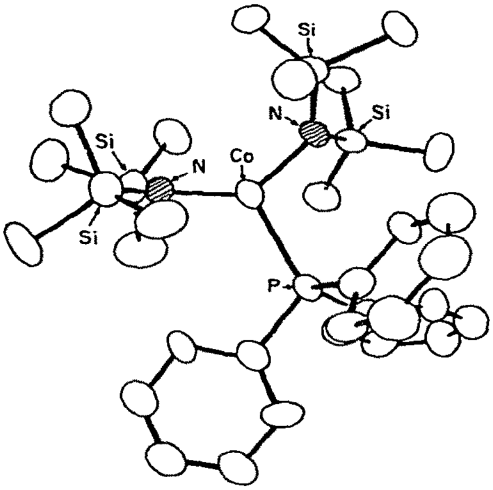


Fig. 5. $Co[N(SiMe_3)_2]_2(PPh_3)$ viewed nearly perpendicular to the CoN_2P plane.

several molecules of THF (perhaps an unstable octahedral 1 : 4 complex exists), but no stable complex has yet been isolated.

A reactive green crystalline complex $Co[N(SiMe_3)_2]_2[P(C_6H_5)_3]$ was isolated from the reaction of $CoCl_2[P(C_6H_5)_3]_2$ and $LiN(SiMe_3)_2$; a single crystal X-ray analysis proved that it was an authentic three-coordinate Co(II) complex [35]. Discussion of the structural parameters (Fig. 5 and Table 6) is deferred for comparison with the Co(II) and Ni(I) complexes in Section IIc. Although the complex was thermally unstable (failed to sublime in vacuo) it

TABLE 6

Some molecular geometry parameters for mixed silylamide-phosphine complexes of Co and Ni

Compound		$Co[N(SiMe_3)_2]_2$-PPh_3	$Co[N(SiMe_3)_2]$-$(PPh_3)_2$	$Ni[N(SiMe_3)_2](PPh_3)_2$
M—N	(A)	1.934(8) 1.917(8)	1.924(8)	1.870(8)
M—P	(A)	2.472(3)	2.257(3) 2.251(3)	2.222(3) 2.209(3)
N—M—N	(°)	131.0(3)		
N—M—P	(°)	117.7(2) 111.2(2)	128.9(2) 124.1(2)	130.3(2) 122.8(2)
P—M—P	(°)		106.5(2)	106.8(2)
N—Si	(A)	1.71(1) 1.73(1) 1.69(1) 1.69(1)	1.66(1) 1.72(1)	1.71(1) 1.71(1)
Si—N—Si		125.5(5)	128.0(5)	125.4(5)

gave a mass spectrum containing the parent molecular ion $CoL_2L'^+$ and the fragment ion CoL_2^+ in low abundance [36]. The compound was paramagnetic and gave μ_{eff} = 4.45 B.M. over the temperature range 98—323 K, and its electronic absorption spectrum in pentane contains bands at 6 750, ~7 500, 11 430, 13 610, 15 150, 16 000 and 23 800 cm^{-1} [36]. In fact, the magnetic moment and the spectra are very similar to those of distorted tetrahedral Co(II) compounds of the type $CoX_2(L')_2$ where the local symmetry is presumably also C_{2v} and crystal field splittings are evidently similar to those in the three-coordinate complex. Fisher [37] has recently shown that $Co[N(SiMe_3)_2]_2$ and $Zn[N(SiMe_3)_2]_2$ also coordinate with pyridine and other N-donor ligands giving 1 : 1 complexes which are presumably three-coordinate.

In an attempt to extend the range of low coordination with bulky uninegative ligands, the reactions of LiL, where L = NC_6H_8 (2,5-dimethylpyrrolyl), with cobalt and nickel phosphine halides were also investigated [36]. A purple, diamagnetic, crystalline compound, $Ni(NC_6H_8)_2[P(C_6H_5)_3]$, was obtained which gave a parent molecular ion in the mass spectrum, but was not stable enough for sublimation. Molecular weight measurements in benzene were somewhat high (590, cf. calc. 508) and X-ray structural evidence is required to establish its authenticity as a three-coordinated complex.

A novel carbon donor complex of the type ML_2L' is the compound $Sn[CH(SiMe_3)_2]_2[Cr(CO)_5]$ obtained by Lappert and co-workers [38]. The crystal structure determination of this compound demonstrated that it contains a three-coordinate tin(II) atom. The bond lengths were found to be: Sn—C 2.18 and Sn—Cr 2.562 Å. The C—Sn—C angle of 98° is surprisingly low, indicating that the $Cr(CO)_5$ group is a very bulky ligand, in spite of the longer Sn—C distance.

(c) Compounds of the type MLL'_2

In this section we deal with the small number of complexes involving three-coordinate univalent metals and hard donor ligands.

The reaction of $NiCl_2[P(C_6H_5)_3]_2$ and $LiN(SiMe_3)_2$ did not give a Ni(II) compound of type $Ni[N(SiMe_3)_2]_2[P(C_6H_5)_3]$ corresponding to the cobalt derivative, but surprisingly gave the Ni(I) complex $Ni[N(SiMe_3)_2][P(C_6H_5)_3]_2$. The pale-yellow, air-sensitive crystals were shown by X-ray single crystal analysis to contain authentic three-coordinate Ni(I) [35]. Although the compound could not be sublimed in vacuo due to dissociation, its mass spectrum showed fragments ions such as $Ni[N(SiMe_3)_2]_2^+$ as well as cluster species of the general formula $Ni_x[N(SiMe_3)_2]_y^+$, (where x = 2, 3, or 4; and $y = x-1$, x, or $x + 1$). Magnetic susceptibilities over the range 98—298 K showed, after correcting for diamagnetism and second-order Zeeman contribution, that the paramagnetic species obeyed the Curie law with μ_{eff} = 1.85 ± 0.03 B.M. [36]. The polycrystalline powder gave EPR signals showing anisotropy ($g_\parallel$ = 2.251 ± 0.003, $g_\perp$ = 2.078 ± 0.003); as did the frozen toluene solution ($g_\parallel$ = 2.257 ±

0.002, $g_\perp = 2.090 \pm 0.002$) which also revealed triplet fine structure due to super-hyperfine coupling of two equivalent phosphorus atoms ($a_\parallel = 61 \cdot 10^{-4}$ cm^{-1}; $a_\perp = 66 \cdot 10^{-4}$ cm^{-1}). The room temperature solution gave the isotropic triplet spectrum ($g_0 = 2.148 \pm 0.002$; $a_{\mathrm{p}31} = 63 \cdot 10^{-4}$ cm^{-1}) [36]. Thus, there is overwhelming evidence that a Ni(I) d^9 complex is present, the bulkiness of the silylamide ligand obviously preventing the formation of a four-coordinate species, e.g., NiL[$P(C_6H_5)_3]_3$, which might be expected by analogy with NiX[$P(C_6H_5)_3]_3$ (X = Cl, or Br). Since the maximum local symmetry is C_{2v}, the apparent axially symmetric EPR signal was surprising, but a slight shoulder on $g_\perp$ may indicate that $g_z \neq g_x \neq g_y$; further work on this system is required. By varying the nature of the phosphine, a series of three-coordinate nickel(I) compounds of type Ni[$N(SiMe_3)_2]L'_2$ [where L' = $PMe_2(C_6H_5)$, $PMe(C_6H_5)_2$, $PEt(C_6H_5)_2$, $PEt_2(C_6H_5)'$, $PtEt_3$ and 1/2$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$] was obtained.

Treatment of CoCl[$P(C_6H_5)_3]_3$ with $LiN(SiMe_3)_2$ gave the rust-brown, very air-sensitive, compound Co[$N(SiMe_3)_2$][$P(C_6H_5)_3]_2$, which could not be sublimed in vacuo and did not give a mass spectrum. Magnetic susceptibility measurements (98—298 K) gave $\mu_{\mathrm{eff}} = 3.50$ B.M., while the infrared spectrum was very similar to that of the nickel analogue [36].

The most important bond lengths and angles in Co[$N(SiMe_3)_2]_2$[$P(C_6H_5)_3$], Co[$N(SiMe_3)_2$][$P(C_6H_5)_3]_2$, and Ni[$N(SiMe_3)_2$][$P(C_6H_5)_3]_2$ are given in Table 6, and the molecular structures are shown in Figs. 5 and 6.

From an examination of the data in Table 6, it is possible to make some general comments. The geometries of the silylamide ligands in each compound are very similar, with fairly short N—Si bond lengths and larger Si—N—Si angles, as compared with sp^2 hybridization. These results suggest that the nitrogen lone-pairs may be involved significantly in N → Si π-bonding and that the

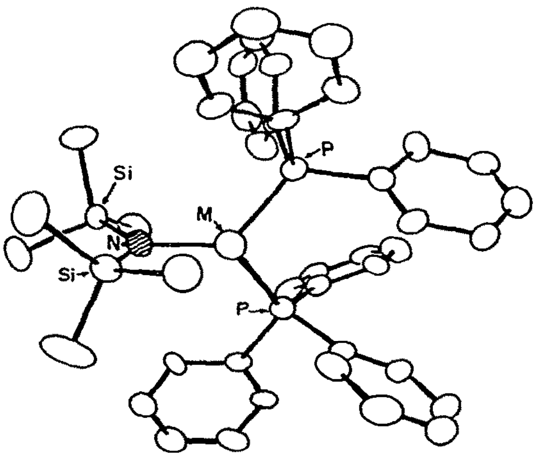


Fig. 6. M[$N(SiMe_3)_2](PPh_3)_2$ (M = Co, Ni); viewed almost perpendicular to the MNP_2 plane.

M—N bond has a degree of ionic character, or possibly M → NSi_2 back-bonding into the N—Si_2 π-system. It is also clear that the silylamide ligand is bulkier that the phosphine ligand (cf. N—M—N, P—M—N, and P—M—P angles) and may also be more strongly bound. These two features could be the cause of the exceptionally long Co—P bond in the Co(II) complex, which, at 2.472 Å is even longer than the sum of the relevant covalent radii. Certainly, the steric interactions between the phosphine and silylamide ligands are quite marked in this compound. This long Co—P bond is to be compared with the M—P bonds in the Co(I) and Ni(I) molecules, which at 2.21—2.26 Å are close to values found in many complexes of Co and Ni with phosphine ligands, and which are taken to indicate metal phosphorus back-bonding.

It is difficult to find a simple explanation for the M—N bond distances in these compounds. The near equality of the Co(II)—N and Co(I)—N bonds may be due to compensation of opposing effects.Thus, the ionic radii are in the order $Co^{2+} < Co^{+}$, but this could be offset by greater metal → phosphorus π-bonding in the Co(I) compound. This is confirmed by the significantly shorter Co—P bond length in the latter. While we should also expect ionic radii in the order $Co^{+} > Ni^{+}$, the short Ni(I)—N bond lengths (compared with the Co(I)—N distance) seems exceptional and may suggest that metal phosphorus π-bonding is stronger in the Ni(I) compound. This view is supported by the M—P bond lengths with Co(I)—P > Ni(I)—P.

The Cu(I) complex $Cu[N(SiMe_3)_2][P(C_6H_5)_3]_2$ was obtained from the reaction of $LiN(SiMe_3)_2$ with $CuCl[P(C_6H_5)_3]_2$. The pale-green needle crystals were diamagnetic and, although they could not be sublimed in vacuo, the mass spectrum showed fragment ions such as $Cu[P(C_6H_5)_3]^+$ and $Cu[N(SiMe_3)_2][P(C_6H_5)_3]$ and cluster species $Cu_x[N(SiMe_3)_2]_y$ (where $x = 3$ or 4; $y = x$ or $x-1$) [36].

Finally, we mention the Ni(I) complex $Ni(NC_6H_8)$ $[P(C_6H_5)_3]_2$ containing the 2,5-dimethylpyrrolyl ligand. This was obtained from the reaction of $LiNC_6H_8$ with $NiCl[P(C_6H_5)_3]_3$ as lime-green crystals which could not be sublimed in vacuo. However, magnetic susceptibilities (98—298 K); ($\mu_{eff} =$ 1.77 B.M.) confirmed the presence of the Ni(I) ion, d^9, and a polycrystalline sample gave a characteristic EPR spectrum ($g_{\parallel} = 2.316 \pm 0.003$; $g_{\perp} = 2.059 \pm 0.003$) [36].

On balance, the crystallographic data suggest that the silylamide ligand does not act as a π-acceptor; it will be very interesting to obtain structural data on low coordination complexes of the 2,5-dimethylpyrrolyl ligand in due course. Other work [36] has indicated the formation of bis-trimethylsilylamide complexes of Mo(III) and Pd(I) in which the metal has a low coordination number, and other new species may be expected in the future.

III. COMPLEXES CONTAINING "SOFT" LIGANDS

In this section we consider three-coordinate complexes containing so-called "soft" ligands. Here the determining factor favoring three-coordination is often electronic in nature, rather than predominantly steric as for the compounds discussed in Section II.

(a) Phosphine, arsine and phosphite complexes

(i) Group VIII metals

Platinum and palladium. The most thoroughly studied three-coordinate complexes of "soft" ligands are those having stoichiometry ML_3, where M is zero-valent nickel, palladium, or platinum and L is a phosphine, arsine, or phosphite ligand. Such ML_3 complexes have been investigated recently as homogeneous catalysts for hydrogenation and isomerization of olefins, and analogies have been made between oxidative-addition reactions involving uncharged ML_3 compounds and chemisorption and catalytic reactions at metal surfaces [39—43].

Several of the PdL_3 and PtL_3 compounds were first prepared by methods rather similar to those used to prepare hydride complexes and before the widespread use of magnetic resonance spectroscopy and X-ray diffraction techniques [44,45]. Consequently, there was suspicion that the ML_3 complexes actually were metal hydrides in which the metal was in a positive oxidation state [46]. However, recent detailed crystallographic and spectroscopic studies confirm that some of the complexes contain zero-valent, three-coordinate metals.

A crystal structure determination of $Pt(PPh_3)_3$ (Fig. 7) revealed a nearly regular trigonal-planar P_3 arrangement around platinum with Pt—P distances in the range 2.25—2.28 Å and with P—Pt—P angles in the range 115—122° [47]. The platinum atom lies 0.1 Å out of the P_3 plane. The observed distortions from ideal trigonal-planar symmetry may be due to crystal packing forces, since a graphite-like packing of phenyl rings in adjacent asymmetric units is present. The corresponding PdL_3 and NiL_3 complexes are also presumed to have trigonal-planar structures.

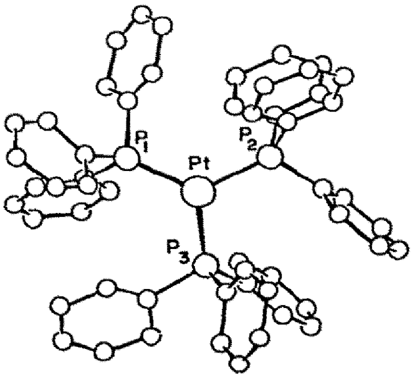


Fig. 7. A perspective of the molecular structure of $Pt(PPh_3)_3$. Adapted with permission from ref. 47. A very similar structure has been reported for the cation $[Au(PPh_3)_3]^+$ (ref. 112).

The first syntheses of ML_3 complexes with palladium (0) and platinum (0) were reported more than fifteen years ago by Malatesta and co-workers [48,49]. The compounds are white to yellow crystalline solids that are soluble in common organic solvents and often air-stable. The compounds may be prepared by a complicated reduction reaction involving tetrachlorometallate salts and excess phosphine in hot, basic aqueous ethanol [42,50]. The ML_3 complexes have also been prepared from the corresponding *cis*-$M(PR_3)_2Cl_2$ complexes, which are intermediates in the reactions involving tetrachlorometallate salts. The ML_n syntheses may also be accomplished using hydrazine as the reducing agent.

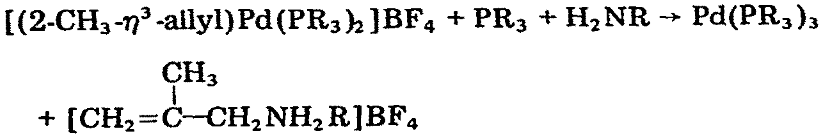
The following mechanism has been postulated to account for the reaction involving tetrachloroplatinate(II) and triphenylphosphine in ethanol [42, 50].

$$\begin{array}{l} K_2PtCl_4 + 2PR_3 \xrightarrow{EtOH(aq)} cis\text{-}[Pt(PR_3)_2Cl_2] + 2KCl \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{KOH, EtOH} \\ \qquad\qquad\qquad\qquad [Pt(PR_3)_2HCl] + KCl + H_2O + CH_3CHO \\ \qquad\qquad\qquad\qquad\qquad \downarrow PR_3\text{, KOH} \\ H_2O + [Pt(PR_3)_3] \leftarrow [Pt(PR_3)_3H]^+ + OH^- + KCl \end{array} \quad (8)$$

The overall reaction is so complex that different products may be isolated at various stages of the reaction, depending upon the temperature, reaction time, concentration of reducing agent, and the specific phosphine or arsine ligand. Thus, other members of the ML_n series (n = 1, 2, 4) and intermediates (e.g., $Pt(PR_3)_2HCl$) may be isolated from the above reaction by judicious choice of conditions. Syntheses of PtL_3 complexes are easiest with the less basic phosphines such as tris(p-chlorophenyl)phosphine or diphenyltrifluoromethylphosphine [51]. Syntheses of $Pd(PR_3)_3$ complexes have also been obtained by direct displacement reactions with palladium(0) isocyanide [48, 52] and π-allyl compounds, e.g., eqn. (9) [53]. Recently a more general synthesis of $Pd(PR_3)_3$ complexes was reported [54]; this involves nucleophilic

$$\begin{array}{l} Pd(p\text{-}CH_3C_6H_4NC)_2 + 3 \text{ (or 4) } (p\text{-}ClC_6H_4)_3P \rightarrow Pd(PR_3)_{3\ (\text{or } 4)} \\ \quad + 2\, p\text{-}CH_3C_6H_4NC \end{array} \quad (9)$$

attack by a primary amine on a π-allyl ligand to give an allylamine, which is subsequently replaced by a tertiary phosphine (eqn. 10).



$$\begin{array}{l} [(2\text{-}CH_3\text{-}\eta^3\text{-allyl})Pd(PR_3)_2]BF_4 + PR_3 + H_2NR \rightarrow Pd(PR_3)_3 \\ \quad + [CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2NH_2R]BF_4 \end{array} \quad (10)$$

Mixed isocyanide—phosphine complexes, which are nominally three-coordinate, have also been obtained by similar reactions [48].

Treatment of triarylphosphines and phosphites with palladium oxide or hot solutions of palladium(II) nitrate is also reported to give PdL_n complexes [48] (eqns. 11,12).

$$PdO + (n + 1)P(OR)_3 \rightarrow Pd[P(OR)_3]_n + (RO)_3PO \ (n = 3, 4) \qquad (11)$$

$$Pd(NO_3)_2 + (n + 5)PR_3 \rightarrow Pd(PR_3)_n + N_2O + 5R_3PO \ (n = 3, 4) \qquad (12)$$

All members of the ML_n series (M = Ni, Pd, Pt) are labile in solution, and complicated equilibria are indicated by studies of the solution (equilibria 13) [51,55,57].

$$ML_4 \underset{+L}{\overset{-L}{\rightleftharpoons}} ML_3 \underset{+L}{\overset{-L}{\rightleftharpoons}} ML_2 \underset{+L}{\overset{-L}{\rightleftharpoons}} [ML]_n \qquad (13)$$

A convenient synthesis for ML_3 complexes utilizes this general lability. For example, the tetrakis(triphenylphosphine)platinum(0) complex is converted to the tris compound simply by refluxing it in hot ethanol [42]. Also, addition of one equivalent of phosphine to solutions of the corresponding 2 : 1 complex favors the 3 : 1 complex.

The labile nature of the system represented by eqn. (13) was convincingly demonstrated recently for tris(diphenyltrifluoromethylphosphine)platinum(0) [51]. The ^{19}F spectrum of this tris(phosphine) complex shows that only one principal species, PtL_3, is present over the observed temperature range of -90 to $+33°C$. The single broad resonance observed at room temperature is due to a phosphine exchange which is rapid on the NMR time scale; such exchange has been observed also for other platinum(0)—phosphine complexes. The exchange was confirmed by adding 0.5, 1, 2 and 5 molar equivalents of the phosphine to a solution of PtL_3 (Fig. 8) [51].

The ML_3 complexes (M = Pd, Pt) are coordinatively unsaturated molecules and react with a variety of Lewis bases in solution to give three- and four-coordinate metal(0) complexes [42]. Due to the lability of the ML_3 compounds, however, it is usually difficult to identify the reactive metal substrate in solution. For example, solutions of $Pt(PPh_3)_3$ react with two moles of carbon monoxide with displacement of one phosphine to give the four-coordinate product $Pt(PPh_3)_2(CO)_2$ [42,49,58]. The "reactive complex" in this reaction could be either $Pt(PPh_3)_3$ or $Pt(PPh)_2$, which could be formed in solution from the tris complex. The latter has been implicated by kinetic studies [59]. Under

$$Pt(PPh_3)_3 + 2CO \rightleftharpoons Pt(PPh_3)_2(CO)_2 + PPh_3 \qquad (14)$$

similar conditions, a four-coordinate complex, $Pt(PR_3)_2(CO)_2$, may be prepared using tri(*p*-chlorophenyl)phosphine. In contrast to the triphenylphosphine com-

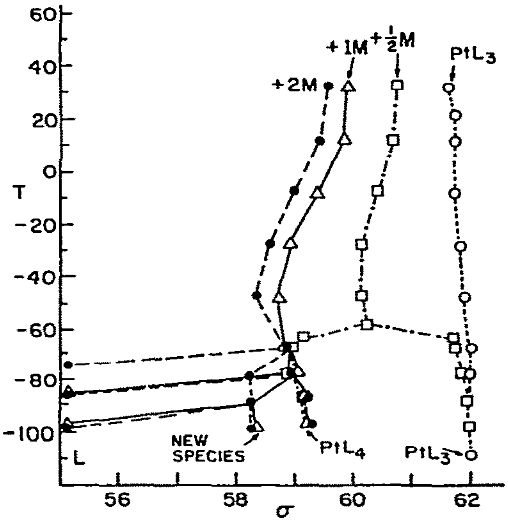


Fig. 8. Fluorine-19 chemical shift data for dichloromethane solutions of $Pt[P(CF_3)(C_6H_5)_2]_3$ and $P(CF_3)(C_6H_5)_2$ over the temperature range +37 to −110°C. Reproduced with permission from ref. 51.

plex, the $Pt[P(C_6H_4\text{-}p\text{-}Cl)_3]_2(CO)_2$ complex dissociates one PR_3 ligand in ether solution, presumably to give the three-coordinate complex $Pt(PR_3)(CO)_2$. Analogous tris-phosphite complexes fail to react with carbon monoxide; this may indicate a reduced tendency to dissociate a $P(OR)_3$ ligand to form $Pt[P(OR)_3]_2$. The $Pt(0)—P(OR)_3$ complexes are apparently more stable than analogous $Pt—PR_3$ complexes, as arylphosphines are displaced by arylphosphites.

Solutions of PdL_3 and PtL_3 complexes react readily in an oxidative—addition fashion to give planar platinum(II) and palladium(II) complexes (eqn. 15).

$$X—Y + PtL_3 \rightleftharpoons PtL_2(X)(Y) + L \qquad (15)$$

Molecules that oxidatively add to PtL_3 include $RSO_2—Cl$, $RCO—Cl$, $H—X$, X_2, O_2 [60—64]; $HS—H$, $HSe—H$, $R—X$ [65—66]; and $L_nM—X$, $(R_3P)Au—Cl$ [42,67,63,62,68,72].

The ML_3 complexes undergo displacement of one phosphine ligand in the presence of a variety of other monodentate ligands to give nominally three-coordinate products (eqn. 16).

$$PtL_3 + L' \rightarrow L + PtL_2L' \qquad (16)$$

π-Bonding ligands such as alkenes [42,73], alkynes [74], CO, O_2 and CS_2 [69,70], as well as σ-bonding ligands such as $(CF_3)_2CO$, H_2S and H_2Se give the displacement reactions. A large series of nominally three-coordinate complexes of the type $M(PR_3)_2L$, where L is a π-bonding ligand such as an olefin,

TABLE 7

Structural data on olefin complexes of types ML_2(olefin) and ML(olefin)$_2$ that are not discussed in detail in the text. Coordination around the metal is trigonal if the olefin is treated as a monodentate ligand

Compound	M—L bond distances (Å)	L—M—L bond angles (deg)	Dihedral angle between ML_2 and M(olefin) planes (deg)	Comments on the structure	Ref.
$[Ni(PPh_3)_2(C_2H_4)]$	Ni—P; 2.147, 2.157(4) Ni—C; 1.98(1), 2.00(1)	P—Ni—P; 110.5(2)	5.0(1)	Olefin C—C bond distance; 1.43(1) Å	a
$\{Ni(P(O\text{-}o\text{-}tolyl)_3]_2(C_2H_4)\}$	Ni—P; 2.093, 2.098(2) Ni—C; 1.99, 2.04(2)	P—Ni—P; 116.3(2) P—Ni—C; 100.3, 101.1(6)	6.6(1)	Olefin C—C bond distance; 1.46(2) Å	b
$\{Ni(P(O\text{-}o\text{-}tolyl)_3]_2(Acryl)\}$	Ni—P; 2.096, 2.121(4) Ni—C; 1.911, 2.016(10)	P—Ni—P; 110.3(1) P—Ni—C; 97.0, 109.2(1)	3.9(1)	Acryl = acrylonitrile; C—C bond distance = 1.46(2) Å; trigonal coordination around Ni.	b
$\{Ni[P(p\text{-}tolyl)_3]_2(Stilbene)\}$	Ni—P; 2.175, 2.186(4) Ni—C; 2.030; 2.008(13)	P—Ni—P; 118.6(2) P—Ni—C; 100.3(4) (av)	18.5(9)	C—C bond distance; 1.47(2) Å	c
$\{Ni[P(C_6H_{11})_3](C_2H_4)_2\}$	Ni—P; 2.196(2) Ni—C; 1.987—2.042(10)	P—Ni—C; 95.8, 96.5(3) P—Ni—C; 135.8, 137.9(3) P—Ni—C; 127.6, 126.3(4)		Planar $NiP(C_2H_4)_2$ core, and both ethylene molecules are in the plane; C—C = 1.41(1) Å	d
$[Ni(CNCMe_3)_2(TCNE)]$	Ni—C; 1.868, 1.864(5) Ni—C; 1.956, 1.951(4)	C—Ni—C; 98.9(2) C—Ni—C; 108.0, 103.5(2)	23.9(2)	$CNCMe_3$ = t-butyl isocyanide and TCNE = tetracyanoethylene; the top row of data are for the $CNCMe_3$ ligands and second row are for TCNE ligand	e
$Ni(R_2PCH_2CH_2PR_2)(Me_4C_2)$	Ni—P; 2.152, 2.160(1) Ni—C; 1.980, 1.981(2)	P—Ni—P; 91.8(1) P—Ni—C; 112.7, 114.8(1) C—Ni—C; 42.0	16.5	R = cyclohexyl; olefin C—C bond = 1.421(3) Å	f

$\{Ni[P(p\text{-tolyl})_3]_2(N_2Ph_2)\}$	Ni—P; 2.195, 2.101(3) Ni—N; 1.927, 1.932(5)	P—Ni—P; 107.4(1) P—Ni—N; 105.2, 105.9(4)	7.6	NiN_2P_3 core within 0.14 Å; trigonal coordination around Ni if azobenzene is regarded as one ligand	g
$[Ni(CNR)_2(N_2Ph_2)]$	Ni—C; 1.841(5) (av) Ni—N; 1.898(4) (av)	C—Ni—C; 101.8 C—Ni—N; 107.6, 107.8	1.2(3)	R = t-butyl; the N—N bond distance in the azobenzene group = 1.385(5) Å, i.e., very close to an NN single bond value	h
$[Ni(PPh_3)_2(\pi\text{-}C_6H_{11})]ZnCl_3$	Ni—P; 2.235, 2.220(4) Ni—C; 2.04, 2.13(3) Ni—C_{middle}; 1.98(3)	P—Ni—P; 102.2(1) C—Ni—C; 71.2(5)		$\pi\text{-}C_8H_{11}$ = the 1,1,2-trimethylallyl group	i
$[Pt(PPh_3)_2(C_2Ph_2)]$	Pt—P; 2.27, 2.28 Pt—C; 2.01, 2.06	P—Pt—P; 102	14	Olefin CC bond length = 1.32 Å	j
$[Pt(PPh_3)_2(C_2H_4)]$	Pt—P; 2.27(1) Pt—C; 2.11(1)		1.3	C—C bond distance; 1.43 Å; trigonal coordination about platinum	k
$[Pt(PPh_3)_2(C_3Ph_3)]$	Pt—P; 2.285, 2.322(3) Pt—C_{end}; 2.09(1) Pt—C_{middle}; 2.48(1)	P—Pt—P; 104.5(1) P—Pt—P_{end}; 104.3, 106.6(3)	6.8	The triphenylcyclopropenyl cation is bonded asymmetrically	l
$[Pt(PPh_3)_2(C_4F_6)]$	Pt—P; 2.277, 2.285(1) Pt—C; 2.024, 2.031(5)	P—Pt—P; 100.17(4) P—Pt—C_{end}; 109.8, 114.1(2)	3.6	Coordination around Pt is trigonal, and the hexafluorobut-2-yne ligand *CC bond has* been lengthened ~0.05 Å to 1.255(9) Å on coordination	m-
$[Pt(PPh_3)_2(\pi\text{-}CS_2)]$	Pt—P; 2.24, 2.35(1) Pt—C; 2.06(4) Pt—S; 2.33(1) C—S; 1.72, 1.54(5)	P—Pt—P; 107(1.5) C—Pt—S; 46(1.5) P—Pt—C; 100(1.5) P—Pt—S; 108(1.5) S—C—S; 136(1.5)	6	The CS_2 group is bonded asymmetrically, and it is essentially coplanar with the Pt and P atoms. Coordination geometry around Pd is trigonal if the C=S linkage is viewed as one ligand position	n

TABLE 7 (continued)

Compound	M—L bond distances (Å)	L—M—L bond angles (deg)	Dihedral angle between ML_2 and M(olefin) planes (deg)	Comments on the structure	Ref.
$[Pd(PPh_3)_2(\pi\text{-}CS_2)]$	Pd—P; 2.316, 2.415(8) Pd—C; 2.00(3) Pd—S; 2.305(11)	P—Pd—P; 108.8(3) C—Pd—S; 44(1) P—Pd—S; 108.3(4) S—C—S; 140(2)		The two C—S bond lengths in the CS_2 unit are 1.65 and 1.63(3) Å	o
$\{Pd(PPh_3)_2[C_2(CO_2Me)_2]\}$	Pd—P; 2.321, 2.330(2) Pd—C; 2.051, 2.074(6)	P—Pd—P; 107.4(6) P—Pd—C; 110.4, 106.2(2)	9.7(4)	Coordination around Pd is essentially planar	p
$[Cu(C{\equiv}CPh)(PMe_3)]_4$	Cu—P; 2.238, 2.222(5) Cu_{trig}—C; 1.96, 2.07, 2.06, 2.09(1) Cu_{tetra}—C; 2.22, 2.11(1)	C—Cu_{trig}—C; 114.0(6), 129.7, 116.5 P—Cu_{tetra}—P; 123.8(2)		The tetrameric structure contains two tetrahedral Cu atoms and two trigonal Cu atoms, which are bonded about equally to three ethynyl groups	q
$[Ag(indene)(ClO_4)]_2$	Ag—C; 2.47(2), 2.36(2) Ag—O; 2.46(2)	O—Ag—C; 116.0, 109.3(4)		Geometry around Ag is trigonal planar with the two aromatic parts and an oxygen of a perchlorate as ligands	r

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acetylene, or a diazo group, have been studied. Most examples that have been studied by X-ray diffraction are listed in Table 7. Reviews of these olefin complexes have appeared [42,73]. Hence, we present only brief and general comments on these nominally three-coordinate $M(PR_3)_2L$ complexes.

(1) All the examples are neutral complexes involving the d^{10} metals Ni, Pd, or Pt.

(2) Almost all examples involve a symmetrically π-bonded ligand L.

(3) The π-ligand atoms lie very close to the MP_2 plane, but small deviations, are the rule rather than the exception.

(4) For a series of comparable ligands, the olefin geometries in the complexes are very similar.

Nickel. Preparation of $Ni(PR_3)_3$ compounds requires stronger reducing agents than for the analogous platinum and palladium compounds; the best yields (~ 50%) are obtained with trimethylaluminum or sodium sand as the reducing agent. Other trialkylaluminum, as well as sodium borohydride and sodium naphthalide, are also effective reducing agents for synthesizing $Ni(PR_3)_3$ compounds [42,60]. Phosphite ligands give analogous $Ni[P(OR)_3]_4$ and $Ni[P(OR)_3]_3$ complexes (OR = OMe, OEt, OPh, OCH_2CCl_3, OC_6H_4-*p*-Cl, and OC_6H_4-*p*-CH_3) [55].

Generally, tetrakis(phosphite)nickel(0) compounds are colorless whereas the tris products are red or violet [75—77]. The tris and tetrakis compounds of nickel(0) are thermally stable, crystalline materials, but they are chemically much more reactive than the corresponding platinum(0) and palladium(0) compounds. The $Ni(PR_3)_3$ complexes react readily with many π- and σ-bonding ligands, including such weak ligands as dinitrogen (eqn. 17).

$$Ni(PR_3)_n + L \rightarrow Ni(PR_3)_2L + (n-2)PR_3 \quad (n = 3, 4) \qquad (17)$$

As with the palladium(0) and platinum(0) compounds discussed above, the nickel(0) complexes are labile and identification of reactive species in solution is very difficult. Excess carbon monoxide displaces all the phosphines to give $Ni(CO)_4$ [42].

Dinitrogen gas reacts reversibly with solutions of $Ni(PCy_3)_3$ (Cy = cyclohexyl) to give the deep-red, dinuclear complex $[Ni(PCy_3)_2]_2N_2$ [78]. A dinuclear structure with a linear dinitrogen bridge (Figs. 9 and 10) was proposed

$$2Ni(PCy_3)_3 + N_2 \rightarrow (Cy_3P)_2Ni{-}N{\equiv}N{-}Ni(PCy_3)_2 + 2PCy_3 \qquad (18)$$

on the basis of spectroscopic evidence; this structure has been confirmed by X-ray crystallography (Fig. 10) [79,80]. Each nickel atom is three-coordinate and has a planar, nearly trigonal coordination environment consisting of two phosphines and one end of the bridging dinitrogen ligand. The Ni—N distances are short (1.77, 1.79 Å) and the angles at nitrogen (178.2, 178.3°) are essentially linear. The N—N distance, 1.12 Å, is slightly longer (as

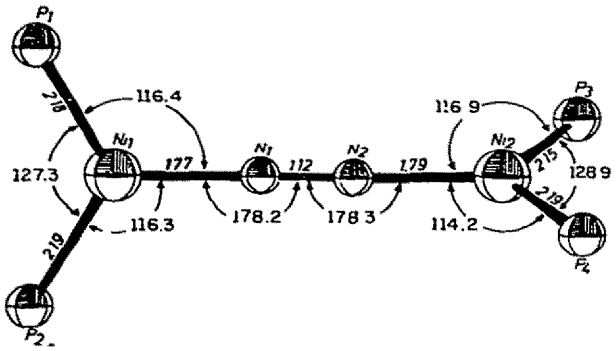


Fig. 9. A view perpendicular to the Ni—N≡N—Ni bond in $[Ni(PCy_3)_2]_2N_2$. Adapted with permission from ref. 80.

expected) than in free N_2 (1.098 Å) and in the usual range (1.12—1.16 Å) for "end-on" bonded dinitrogen groups. An interesting feature of the structure is the cage-like arrangement of two cyclohexyl groups about the dinitrogen bridge which provides a protective environment that may contribute to the stability of the complex [79,80]. Another interesting structural feature is the perpendicular orientation of the two NiP_2N planes, which is the arrangement that is most favorable for π-backbonding into both π^* orbitals of the dinitrogen ligand.

Molecular weight and infrared data indicate that $[Ni(PCy_3)_2]_2(N_2)$ dissociates in benzene solution to give the mononuclear, three-coordinate dinitrogen complex, $Ni(PCy_3)_2(N_2)$. Unfortunately, structural data are not

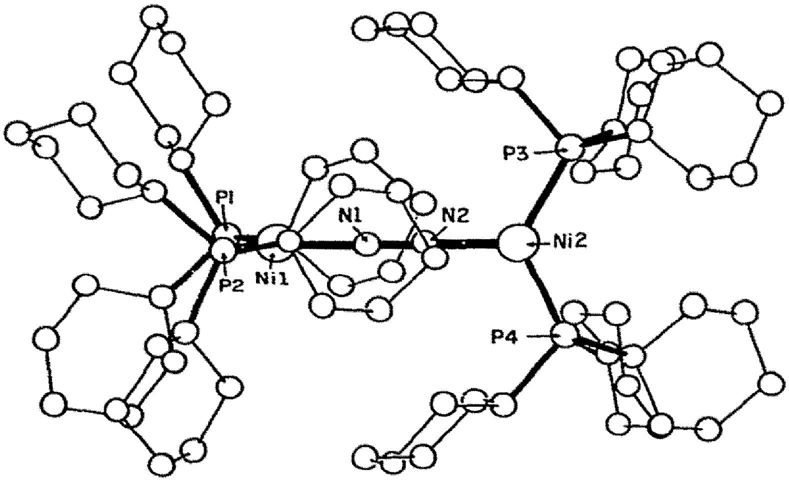


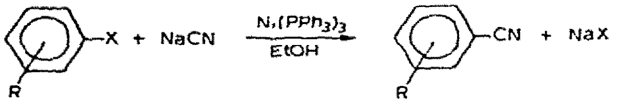
Fig. 10. A perspective of the molecular structure of $[Ni(PCy_3)_2]_2N_2$ which shows the effective packing of the cyclohexyl groups around the Ni—N≡N—Ni bond. Adapted with permission from ref. 80.

available on the mononuclear compound. The dinitrogen ligand in both of the mononuclear and dinuclear nickel complexes is easily displaced by olefins and other ligands [78].

Attempts to prepare a dinitrogen complex of nickel by using triethylaluminum in the presence of ethylene gave the well-known π-ethylene complex $Ni(PR_3)_2(C_2H_4)$. This compound, however, is converted to $[Ni(PCy_3)_2]_2(N_2)$ in a stream of dinitrogen gas at 100°C. The reaction is accelerated by the presence of added phosphine, which suggests that some $Ni(PCy_3)_3$ may be formed and that the latter is the reactive species with N_2 (eqn. 19).

$$Ni(PCy_3)_2(C_2H_4) + PR_3 \xrightarrow[-C_2H_4]{100^\circ C} Ni(PCy_3)_3 \xrightarrow[N_2]{25^\circ C} 1/2[Ni(PCy_3)_2]_2(N_2) + PCy_3 \qquad (19)$$

Tris (triphenylphosphine)nickel(0) is an effective catalyst [81] for converting aryl halides into the corresponding nitriles at temperatures as low as 30°C, in comparison to the 150—240°C usually needed for the reaction (eqn. 20).



(20)

The rate of nitrile formation depended on the aryl group substituent in the order: $p\text{-}OCH_3 > p\text{-}CH_3 > H \sim m\text{-}CH_3 > p\text{-}COCH_3 > o\text{-}C_4H_4 > o\text{-}CH_3\ o\text{-}F \gg o\text{-}Cl, o\text{-}CN$. It is known that aryl-nickel complexes react with sodium cyanide to produce aromatic nitriles and nickel(0) complexes; also, aromatic halides oxidatively add to nickel(0). Thus, a reasonable catalytic cycle is initial oxidative addition of the aromatic halide to tris(triphenylphosphine) nickel(0) followed by cyanation of the aryl-nickel(II) complex (eqn. 21).

$$trans\text{-}Ni(PPh_3)_2(aryl)Cl + NaCN + PPh_3 \rightarrow aryl\text{—}CN + Ni(PPh_3)_3 + NaCl \qquad (21)$$

Additional support for this sequence is provided by the observation that both $Ni(PPh_3)_3$ and *trans*-halo(aryl)-nickel(II) complexes show equal catalytic activity. Also, more basic alkyl phosphines exhibit reduced reactivity or do not react at all.

Gosser and Tolman [82] prepared the three-coordinate Ni(0) complex $Ni[P(OC_6H_4\text{-}o\text{-}CH_3)_3]_3$ and used it to isolate mixed ligand, nominally three-coordinate phosphine—olefin complexes of the type $Ni[P(OC_6H_4\text{-}o\text{-}CH_3)_3]_2$ (olefin), where olefin = ethylene, maleic anhydride, acrylonitrile, styrene, propylene, and 1,5-cyclooctadiene [83,84]. The degree of phosphine or phosphite dissociation in the tris complexes is apparently determined more by steric than by electronic factors. For example, the dissociation constant, K_d

is ~10^{-7} times smaller for tri(*p*-tolyl)phosphine than for the more bulky but electronically similar ligand tri(*o*-tolyl)phosphine [83]. The ligand-association equilibrium constant for adding a fourth tri-*o*-tolylphosphite ligand (eqn. 22) was 15 ± 2 M^{-1} in benzene at 28°C [83]. The temperature dependence of equilibrium (22) gave $\Delta H^0 = -13 \pm 1.5$ kcal mol^{-1} and $\Delta S^0 = -37 \pm 4$ eu. Although the tris-phosphite complexes $Ni[P(OC_2H_5)_3]_3$ [85] and

$$\mathrm{NiL_3 + L} \underset{L\,=\,\text{tri-}o\text{-tolylphosphite}}{\rightleftharpoons} \mathrm{NiL_4} \qquad (22)$$

$Ni[P(OC_6H_4\text{-}p\text{-}OCH_3)_3]_3$ were proposed [86] as steady state intermediates in kinetic studies of ligand substituent reactions of the tetrakis complexes, the concentrations of the three-coordinate complexes must be very small, as Gosser and Tolman [82] found no detectable concentrations of NiL_3 species in solutions of $Ni[P(OC_2H_5)_3]_4$ or $Ni[P(OC_6H_4\text{-}p\text{-}OCH_3]_4$. The isolability of the tris-phosphite and tris-phosphine complexes $Ni[P(OC_6H_4\text{-}o\text{-}CH_3)_3]_3$ and $Ni(PPh_3)_3$ probably results from the large steric requirements of these two ligands, whose cone angles are 165° and 145°, respectively.

Spectrophotometric measurements show that addition of tri-*o*-tolylphosphite to a solution of $Ni[P(OC_6H_4\text{-}o\text{-}CH_3)_3]_2(C_2H_4)$ rapidly converts it to tris- and tetrakis(tri-*o*-tolylphosphite)nickel(0) complexes. The equilibrium constant for the reaction represented by eqn. (23) has a value of $6.8 \pm 0.5 \cdot 10^{-3}$ in benzene at 28°C and indicates that ethylene is preferred to *o*-tolylphosphite in bonding to NiL_2 by a factor of about 150 [82].

$$\mathrm{(C_2H_4)NiL_2 + L \rightleftharpoons NiL_3 + C_2H_4} \qquad (23)$$

Other $Ni[P(OC_6H_4\text{-}o\text{-}CH_3)_3]_2$ (olefin) complexes can be conveniently prepared by displacement of complexed ethylene [84]. Tolman [87] determined the equilibrium constants for the reaction of 38 olefins with $Ni[P(OC_6H_4\text{-}o\text{-}CH_3)_3]_3$ in benzene at 25°C (eqn. 24). The values of K_{eq} vary

$$\mathrm{NiL_3 + olefin} \overset{K_{eq}}{\rightleftharpoons} \mathrm{(olefin)NiL_2 + L} \qquad (24)$$

tremendously, from 10^{-4} to $4 \cdot 10^8$, depending on the olefin. Electron-withdrawing substituents (e.g., carboxyl or cyano) on acyclic olefins give more stable olefin complexes, with resonance effects being more important than inductive effects and steric effects being minor.

When compared to equilibrium studies with other metals, the Ni(0) equilibrium constants are extremely sensitive to structural modification of the olefins. For each alkyl substituent on ethylene, K_{eq} (eqn. 24) decreases by factors of approximately 3, 20 and 300, respectively, for Ag(I), Rh(I) and Ni(0) metal centers. This sensitivity has been rationalized [87] by a model that considers the bonding interaction between the metal center and the olefin to involve primarily the highest occupied π-molecular orbital (HOMO) of the olefin and the lowest unoccupied molecular orbital (LUMO)

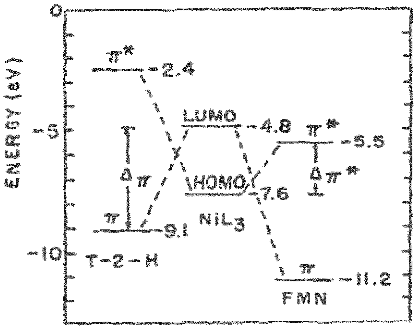
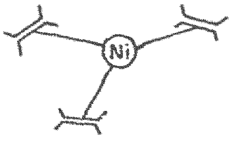


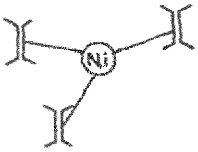
Fig. 11. Energy level diagram showing the relative positions of the highest occupied and lowest unoccupied MO's of Ni[P(O-*o*-tolyl)$_3$]$_3$, *trans*-2-hexene(T-2-H) and fumaronitrile (FMN). Reproduced with permission from ref. 87.

of the metal complex, with an additional interaction of the ML$_3$ HOMO with the olefin π^* LUMO. This corresponds to the Dewar—Chatt—Duncanson [88] picture of donation of olefin electrons to the metal and metal electron donation to the olefin. Figure 11 illustrates the relative nature of these interactions for *trans*-2-hexene and fumaronitrile. As the metal HOMO is lowered in the series Ni(0) $\geqslant$ Fe(0) $\geqslant$ Pt(0) > Rh(I) > Pt(II) > Ag(I), the separation $\Delta\pi^*$ is increased, resulting in less electron donation from metal to olefin π^*. Thus, as the magnitude of interaction decreases, the selectivity of the metal for specific olefins is reduced.

Interestingly, the same type of π back-bonding ideas were used by Rösch and Hoffmann [90] in a molecular orbital calculation that indicated the "all-planar" Ni(C$_2$H$_4$)$_3$ structure (A) was more stable than an "all-upright" geometry (B). Indeed X-ray studies on some tris-olefin complexes of more complicated olefins do show structure A



A, D_{3h}



B, D_{3h}

ESCA measurements on the NiL$_2$(olefin) complexes support a loss of electron density from the metal center [89]. Larger values of the NMR shift for the olefinic protons and smaller values of the C—C stretching frequency indicate greater electron donation from metal *d*- to olefin π^*-orbitals [91], which in turn should reduce the C=C bond order. Comparative spectral and structural data for a series of ethylene complexes are given in Table 8. The Ni[P(O-*o*-tolyl)$_3$]$_2$(C$_2$H$_4$) complex has the highest chemical shift, lowest C=C stretching frequency, and longest C—C bond distance among the different

TABLE 8

Physical characterization data on ethylene oxide and transition metal complexes of ethylene *

Compound	τ	ν_{C-C} (cm^{-1})	d_{C-C} (Å)	Ground state IP of atomic M^+, (eV)
Ethylene oxide	7.2	1487	1.472	13.6
$Ni[P(O\text{-}o\text{-tolyl})_3]_2(C_2H_4)$	8.1	1487	1.46(2)	7.6
$Fe(CO)_4(C_2H_4)$	7.5	1510	1.46(6)	7.9
$Pt[P(C_6H_5)_3]_2(C_2H_4)$	7.4		1.43	9.0
$Rh(acac)(C_2H_4)$	6.9	1524	1.41(3)	18.1
$PtCl_3(C_2H_4)^-$	5.3	1526	1.35(1)	18.6
$Ag(C_2H_4)^+$	4.3	1583		21.5
C_2H_4	4.7	1623	1.337(3)	

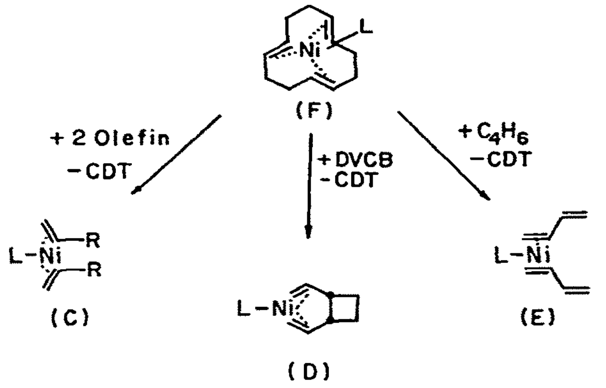
* Data from Table IV, 2779 of C.A. Tolman and W.C. Seidel, J. Am. Chem. Soc., 96 (1974) 2774.

metal complexes; in fact, ethylene in $NiL_2(C_2H_4)$ resembles the ethylene oxide molecule. As the ability of the metals to π back-bond decreases in the series Ni(0) > Fe(0) ~ Pt(0) > Rh(I) > Pt(II) > Ag(I), values of τ, $\nu_{C=C}$, and $d_{C=C}$ tend to approach those of the free olefin. Table 8 also shows that a decreasing π back-bonding ability of the metal correlates with increasing ionization potential for the isolated atom or ion. The ionization potential of the metal and its ability to back-bond are, of course, changed by its ligands; however, the large changes in the spectral and structural parameters and the correlations with ionization potential shown in Table 8 appear significant.

Wilke's studies on olefin—Ni(0) complexes gave a large number of bis(olefin)—nickel(0) complexes by displacement of cyclododecatriene from its Ni(0) complex [92,93]. For example, the nearly white compound tricyclohexylphosphine-bis(ethylene)Ni(0) is formed in 80—90% yield when ethylene is passed through a suspension of *all-trans*-1,5,9-cyclododecatrienecyclohexylphosphinenickel(0) in ether at —20°C [93]. Similar reactions are given in Scheme I.

Three-coordinate nickel(0) complexes containing two olefin molecules are useful butadiene cyclodimerization catalysts [94]. For example, bis(butadiene)tricyclohexylphosphinenickel(0), (D), reacts with excess triphenylphosphine at 80°C to give 65% of the expected butadiene, the rest being dimerized. However, reaction in solution with carbon monoxide at —78°C gives exclusively vinylcyclohexene (VCH) (Scheme II). Although dimerization of butadiene to divinylcyclobutane with a nickel catalyst was proposed as a concerted process [95], Wilke and co-workers [94] have demonstrated that it is a multi-step process. Proton NMR spectra were identical for (G) and (H)

Scheme I



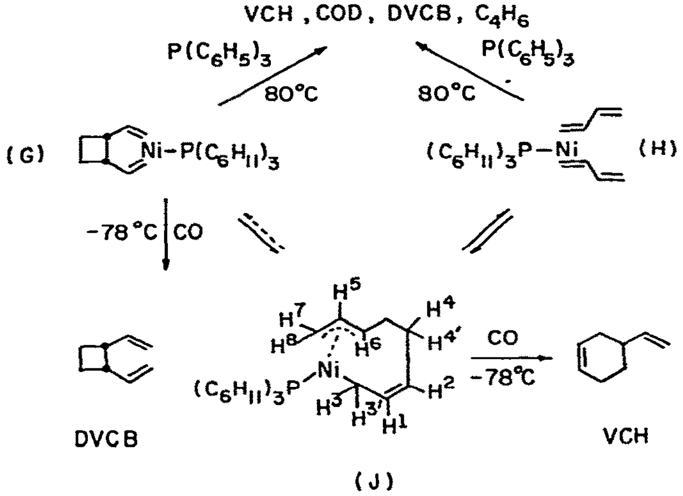
$L = P(C_6H_{11})_3$ for C; R = H, CH_3, or 3-cyclohexenyl

$L = P(C_6H_5)_3$ for D and E

$L = P(C_6H_5)_3$ for C and R=H

in solution, indicating an equilibrium involving the π-allyl—σ-allyl structure (J) (Scheme II). Compound (G) reacts with carbon monoxide at −78°C to

Scheme II



give divinylcyclobutane, but if it is left standing for one hour in solution at room temperature, the product is exclusively vinylcyclohexene. Thus, nickel acts to coordinate butadiene which can then cyclize in a stepwise manner to give the observed vinylcyclohexene.

More detailed comparisons of tris-olefin complexes are made in Section III(f).

Three-coordinate nickel(I)—phosphine complexes may result from dissociation of tetracoordinate species or from electrochemical reduction of Ni(II) phosphine complexes, but none have been characterized by an X-ray structure determination [96]. Heimbach [97] reported the first three-coordinate nickel(I) complexes in 1964. He observed that the four-coordinate complexes $Ni(PPh_3)_4$ and $Ni(PPh_3)_3X$ (X = Cl, Br, I) dissociate in benzene solution to give the three-coordinate complexes $Ni(PPh_3)_3$ and $Ni(PPh_3)_2X$, respectively, in equilibrium with free triphenylphosphine.

Sacco and co-workers recently reported [77] that reduction of $NiX_2(PCy_3)_2$ (X = Cl, Br; PCy_3 = tricyclohexylphosphine) in toluene with sodium sand under argon readily gives either $[NiX(PCy_3)_2]_2$ or $Ni(PCy_3)_3$ in ~50% yields depending on the reaction conditions. If the sodium reduction of $NiX_2(PCy_3)_2$ is done under a nitrogen rather than an argon atmosphere, $[Ni(PCy_3)_2]N_2$ is obtained in 50% yield. On the basis of their electronic spectra and magnetic moments the nominally three-coordinate nickel(I) complexes $[NiX(PCy_3)_2]_2$ (X = Cl, Br) are dimeric in the solid state. However, molecular weight measurements in benzene give monomeric values for both compounds; thus, the complexes may be three-coordinate in solution. The electronic spectra of the three-coordinate $NiX(PCy_3)_2$ complexes are given in Table 9.

The $NiX(PCy_3)_2$ complexes are reduced easily by sodium sand in toluene at room temperature under argon to give the tris-Ni(0) complex $Ni(PCy_3)_3$ [77]. No $Ni(PCy_3)_4$ is formed, even in the presence of excess PCy_3, presumably because of the large cone angle (179 ± 10°C) [98] of this ligand. The purple, diamagnetic tris complex $Ni(PCy_3)_3$ is air-sensitive, oxidized by halocarbons, and reacts with HCl in ethanol to give the known hydride (eqn. 25).

$$Ni(PCy_3)_3 + HCl \rightarrow NiHCl(PCy_3)_2 + PCy_3 \qquad (25)$$

It reacts with N_2 in the solid state (and in solution) to give the binuclear dinitrogen complex $[Ni(PCy_3)_2]_2N_2$, whose structure was discussed above.

If one starts with nickel(II) complexes of less bulky phosphines (e.g., PR_3

TABLE 9

Electronic absorption data for three-coordinate Ni(0) and Ni(I) complexes of tricyclohexylphosphine

Compound	Absorption max (nm)				
$Ni(PCy_3)_2Cl$ *	290(1260) ***	340(2490)	360(2435)	400(600)	
$Ni(PCy_3)_2Br$ *	290(2346)	340(2453)	360(2406)	400(570)	
$Ni(PCy_3)_3$ **	260	340		420 (sh)	520 max
$[Ni(PCy_3)_2]_2N_2$ **	260	340		400	520 max

* Benzene solution; max: maximum; sh: shoulder; br: broad; w: weak; vw: very weak.
** Solid state in MgO. *** Molar extinction coefficient in parentheses.

= $P(C_2H_5)_3$, $P(n\text{-}C_4H_9)_3$, $P(C_2H_5)_2(C_6H_5)$), the tetracoordinate Ni(0) complexes $Ni(PR_3)_4$ are obtained directly. Some of the latter complexes apparently undergo dissociation to tris(phosphine) complexes even in the solid state (eqn. 26) [77,99].

$$Ni(PEt_3)_4 \rightleftharpoons Ni(PEt_3)_3 + PEt_3 \qquad (26)$$

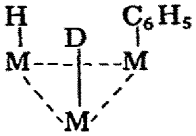
The $Ni(PEt_3)_4$ complex remains white if stored at —20°C; however, at room temperature it converts irreversibly to the violet tris(phosphine) compound $Ni(PEt_3)_3$ (eqn. 26) [55,77,99]. The tetracoordinate complexes $Ni(PR_3)_4$ ($PR_3 = PEt_3$, $P(n\text{-}Bu)_3$, and PEt_2Ph) readily add dinitrogen according to eqn. (27), presumably after undergoing dissociation (indicated by the white to violet color transformation) to the three-coordinate species $Ni(PR_3)_3$.

$$\underset{\text{white}}{Ni(PR_3)_4} \rightarrow PR_3 + \underset{\text{violet}}{Ni(PR_3)_3} \xrightarrow{N_2} Ni(PR_3)_3N_2 + PR_3 \qquad (27)$$

Nominally three-coordinate nickel(I) hydride complexes of the type $HNi(R_2PCH_2CH_2PR_2)$ have been prepared and shown to be diamagnetic and unusually stable thermally (to 250°C) [100]. The diamagnetism rules out a monomeric structure, and an X-ray study on $HNi(Ph_2PCH\cdot CH_2PPh_2)$ showed that it had a dimeric structure with pentacoordinate nickel [100]. The hydrides occupy bridging positions, and a metal—metal bond (2.444 Å) is present. This hydride complex is believed to be a key intermediate in the model for the cleavage of the hydrogen molecule during heterogeneous catalytic hydrogenation at a nickel surface. Other known complexes of the type $Ni(R_2P(CH_2)_nPR_2)X$ (X = Cl, BH_3, BH_4, AlH_3, $AlMe_3$, BPh_3) may also be examples of three coordination, but their structures have not been determined.

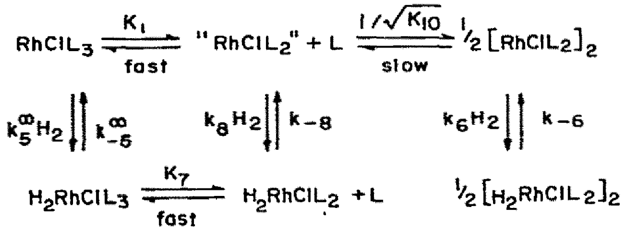
Rhodium and ruthenium. Many papers have been published concerning the uses and limitations of $Rh(PPh_3)_3Cl$, $Rh(PPh_3)_3(CO)H$, $Ru(PPh_3)_3Cl_2$, $Ru(PPh_3)_3HCl$, $Ru(PPh_3)_3H(COOR)$, and similar complexes as homogeneous hydrogenation catalysts [101—103]. In many of the reaction sequences, nominally three-coordinate intermediates are believed to play a key role. In the context of this review, and considering the fact that few such complexes have actually been isolated, the role of three coordination for rhodium and ruthenium catalysts will be emphasized in the following section.

It is concluded that a critical requirement of the rhodium and ruthenium catalysts is a combination of an electron-rich metal center with three polarizable ligands other than hydride. In addition, a homogeneous catalyst should possess the structural feature of three adjacent orbitals on a single metal atom for the three "exchange or reaction sites." In contrast, for heterogeneous catalysis of reactions of aromatic hydrocarbons (e.g., exchange reactions of arene C—H), the three essential sites are thought to be located on three separate metal atoms as shown below [104].



Each of the active hydrogenation catalysts $Rh(PPh_3)_3Cl$, $Rh(PPh_3)_3(CO)H$, $Ru(PPh_3)_3HCl$ and $Ru(PPh_3)_3H(COOR)$ dissociates one or more triphenylphosphine ligands to produce a "three-coordinate active species" (excluding hydride and potentially solvating ligands), i.e., $Rh(PPh_3)_2Cl$, $Rh(PPh_3)_2(CO)H$, $Ru(PPh_3)_2HCl$ and $Ru(PPh_3)_2H(COOR)$, respectively. Halpern and Wong [105] showed that $Rh(PPh_3)_2Cl$, which is formed by dissociation of $Rh(PPh_3)_3Cl$, is at least 10^4 times as reactive as either $Rh(PPh_3)_3Cl$ or the dimer $[RhCl(PPh_3)_2]_2$. In the ruthenium series of catalysts, $Ru(PPh_3)_3^{2+}$ or $[Ru(PPh_3)_2(alkene)]^{2+}$ is the active species from each of complexes $RuH(CO_2CH_3)(PPh_3)_3$, $Ru(CO_2CH_3)_2$ $(PPh_3)_2$, $Ru_3O(CO_2CH_3)_6(PPh_3)_3$, $RuH(CO_2CH_3)(PPh_3)_3$ and $RuH_2(PPh_3)_4$ [106].

The conditions, reactions, and mechanisms for the activity of the Wilkinson catalyst have probably been studied more than for any other homogeneous catalyst [101—103]. The mechanistic details for catalytic hydrogenation, as well as the formula of the "active species" in solutions of $Rh(PPh_3)_3Cl$, have been interpreted in several different ways. However, kinetic studies by Halpern and Wong [105] and King and Bennett [107], along with physical measurements by Tolman et al. [108], provide a fairly consistent picture of the equilibria and the "active species" in solutions of $Rh(PPh_3)_3Cl$. The behavior of the H_2 reaction kinetics are summarized by Scheme III, in which



the three-coordinate or solvated "$RhCl(PPh_3)_2$" species plays a key role. The value of k_8 must be greater than $4 \cdot 10^3$ min^{-1}. In spite of the very low concentration of "$RhCl(PPh_3)_2$", (undetectable spectroscopically), more than 90% of $H_2RhCl(PPh_3)_3$ must be formed by this path in the presence of 0.01 M added triphenylphosphine.

A simple three-coordinate "RhL_2Cl" intermediate does not fit the 16- and 18-electron rule [109a] for reactive species in organometallic reactions; however the rule may not be applicable for kinetic intermediates. For example, Whitesides et al. [109b] presented kinetic evidence for $Pt(PPh_3)_2$, also a 14-

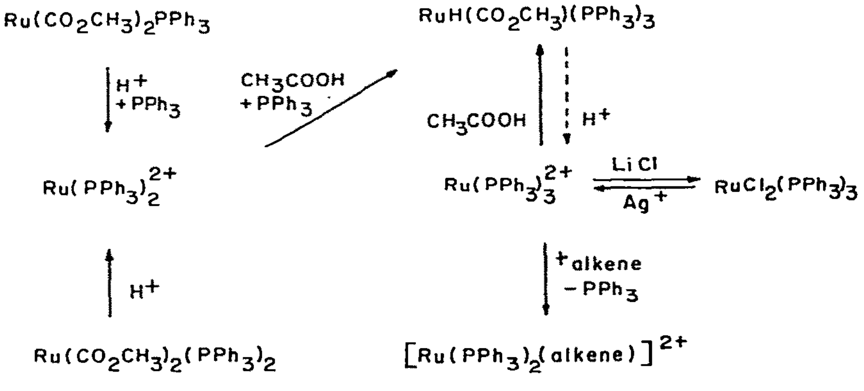
electron species, although it was spectroscopically undetectable in solution.

James and Ng [110] recently reported that $HRh(PPh_3)_4$ catalyzes the hydrogenation of 1-hexene in benzene. The catalyst apparently dissociates triphenylphosphine to give both four-coordinate $HRh(PPh_3)_3$ and three-coordinate $HRh(PPh_3)_2$. Dissociation to $HRh(PPh_3)_2$ is nearly complete at 38°C, even at a 10^{-2} M concentration of complex. The three-coordinate, 14-electron species $HRh(PPh_3)_2$ is the most reactive complex in solution.

Kagan and Dang [111] used the chiral diphosphine ligand DIOP (DIOP = 2,3-*O*-isopropylidene-2,3-dihydroxyl-1,4-bis(diphenylphosphino)butane) with rhodium(I) for asymmetric hydrogenation of olefins. The catalyst $[RhCl((-)\text{-DIOP})(C_6H_6)]$ gives yields of optically active products in the range 70—80% in the reduction of β-substituted α-acetamidoacrylic acids to precursors of alanine, phenylalanine, tyrosine, dopa, and leucine.

Addition of acids to the complexes $RuH(CO_2CH_3)_2(PPh_3)_2$, $RuH_2(PPh_3)_4$, and $Ru(CO_2CH_3)_2(PPh_3)_2$ or electrochemical reduction of the oxo—acetato complex $Ru_3O(CO_2CH_3)_6(PPh_3)_3$ produces a yellow Ru(II) species that is a hydrogenation catalyst for alkenes [106]. The "active species" from these Ru(II) complexes appears to be a three-coordinate, cationic ruthenium(II) complex with two triphenylphosphine ligands, the other coordination sites being occupied by either solvent or coordinated alkene molecules. The catalytic cycle then may proceed by steps generally accepted for other homogeneous catalysts, namely oxidative addition of molecular hydrogen to the cationic alkene complex, hydride transfer to produce an alkane, followed by a second hydride transfer and alkane elimination. The reactions that involve these three-coordinate ruthenium complexes are summarized by Scheme IV.

SCHEME IV



(ii) Group IB metals

ML_3^+ complexes. The structure of a $[M(PR_3)_3]^+$ cation, the structural prototype for this series of complexes, has been determined crystallographically in the salt $[Au(PPh_3)_3][B_9H_{12}S]$ [112]. The structure consists of discrete

carborane anions and approximately trigonal-planar $[Au(PPh_3)_3]^+$ cations which are structurally very similar to the neutral complex $Pt(PPh_3)_3$ (Fig. 7). The metal lies 0.20 Å out of the plane of the three phosphines, the Au—P distances are in the range 2.373—2.389 Å, and the P—Au—P angles are 112.3, 121.5, and 124.1°. The $[Au(PPh_3)_3]^+$ cation is also present in the compound $Au(PPh_3)_{1.5}CN$, properly formulated as the salt $[Au(PPh_3)_3][Au(CN)_2]$. The Au—P distances in the $[Au(PPh_3)_3]^+$ cation are ~0.1 Å longer than the Pt—P distances in the isoelectronic uncharged complex $Pt(PPh_3)_3$ and they are longer than the Au—P distances in two-coordinate gold(I)—phosphine complexes. The Au—P distances in $[Au(PPh_3)_3]^+$, which are the longest yet reported for any gold complex, indicate that little or no Au → π-bonding exists in this complex [113]. The long Au—P bond lengths are consistent with the expectation that the positive charge on the gold atom would reduce the π-backbonding to the phosphine ligands compared to the Pt(0) complex. The $[M(PPh_3)_3][B_9H_{12}S]$ compounds (M = Cu, Ag, Au) are all isomorphous [114]. The observed hydrolytic and oxidative stabilities, along with the relative sensitivities of the copper and gold compounds to X-radiation, indicate the relative stabilities $AuL_3^+ > AgL_3^+ > CuL_3^+$ for the three-coordinate Group IB cations of triphenylphosphine.

Discrete three-coordinate $[CuL_3]^+$ and $[AgL_3]^+$ cations (L = phosphine or arsine) analogous to the neutral ML_3 (M = Ni, Pd, Pt) and cationic $[AuL_3]^+$ complexes have not been proven by X-ray diffraction methods, although a number of CuL_3X compounds have been synthesized (X = Cl, Br, I, NO_3, ClO_4, BF_4). With the exception of complexes containing anions of the very strongest acids, the neutral CuL_3X complexes are tetracoordinate [115,116]. Even in the case of $Cu(PPh_3)_3(BF_4)$, the geometry around copper is pseudotetrahedral, with a fluorine atom from the tetrafluoroborate group (Cu—F = 2.31 Å) as the fourth ligand [117]. The structure of the complex $Cu(PMePh_2)_3(NO_3)$ is pseudotetrahedral [116], similar to that of $Cu(MePh_2P)_3Cl$ [118]. Three-coordinate $Cu(PR_3)_3^+$ cations apparently exist in solution, however, as shown by ^{31}P NMR studies on the complex $[Cu(PPh_3)_3]PF_6$ [115].

In the presence of excess phosphine and weakly coordinating anions such as PF_6^-, ClO_4^-, and BrO_3^-, it is also possible to prepare four-coordinate $Cu(PR_3)_4^+$ and $Ag(PR_3)_4^+$ cations in solution. In the presence of excess PPh_3 and coordinating anions such as Cl^-, NO_3^-, $B_3H_8^-$, and $CF_3CO_2^-$, only neutral, four-coordinate $M(PR_3)_3X$ compounds (M = Ag, Cu) are isolated, however. The 3 : 1 phosphine—silver complexes disproportionate to give both two- and four-coordinate species in solution (eqn. 28).

$$2L_3AgX \text{ (or } L_3Ag^+X^-) \rightarrow L_2Ag^+ + L_4Ag^+ + 2X^- \qquad (28)$$

Some of the complexes also undergo phosphine dissociation at temperatures above −70°C. For example, $(R_3P)_3AgCl$ is almost completely dissociated at room temperature into $(R_3P)_2AgCl$ and R_3P.

The chemical properties of the $M(PR_3)_3^+$ complexes (M = Cu, Ag, Au; PR_3

= phosphine or phosphite) have not been studied extensively, but these compounds appear to exhibit lower chemical reactivity than the corresponding zero-valent $M(PR_3)_3$ compounds (M = Ni, Pd, Pt). These IB complexes show little tendency to bind or to activate small molecules such as H_2, O_2, SO_2, or olefins. Classical two-electron oxidative-addition reactions are unknown for Cu^+ and Ag^+ compounds and known only to a limited extent for Au^+ complexes. This reactivity pattern is due primarily to the instability of the trivalent oxidation state in the presence of soft donor ligands and to the relative stability of the 16-electron configuration for these metals. The reduced reactivity of the ML_3^+ species (M = Cu, Ag, Au) relative to the neutral ML_3 (M = Ni, Pd, Pt) and ML_2XY (M = Co, Rh, Ir) compounds has also been attributed to the decreased nucleophilicity of the metal and to the increased separation between the metal $(n-1)$ and $(n)p$ orbitals [42]. All these factors probably contribute to the minimal catalytic properties observed thus far for Group IB three-coordinate cations, in sharp contrast with the chemical behavior of the neutral, isoelectronic ML_3 complexes.

ML_2X complexes. A large number of neutral ML_2X compounds (L = phosphine or arsine; X = halogen or pseudohalogen) of group IB metals are known. Some are discrete three-coordinate examples, but most achieve four coordination via bridging anions.

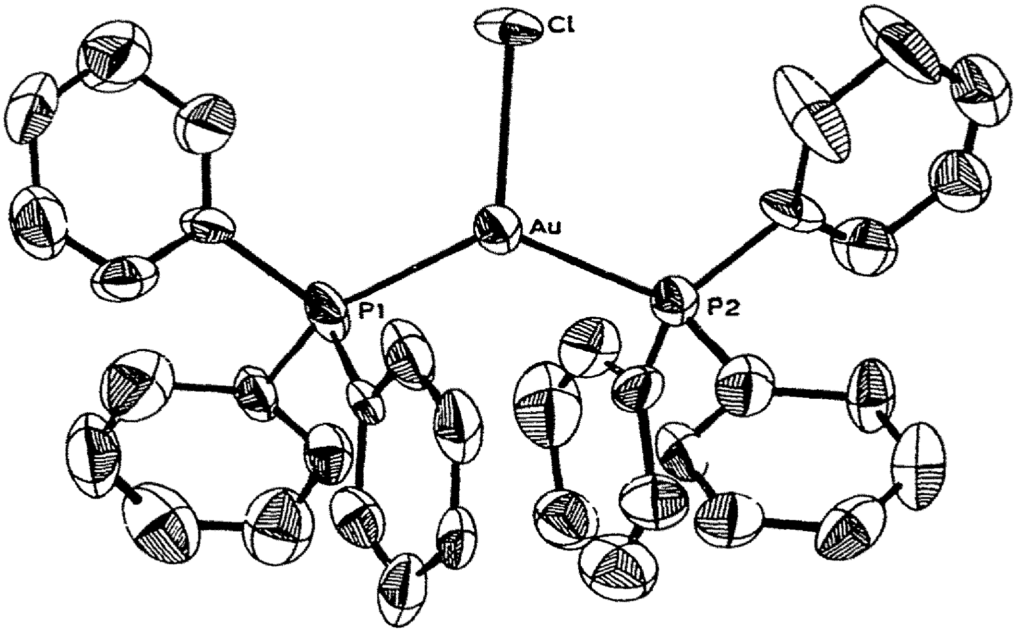


Fig. 12. A perspective of the structure of $[Au(PPh_3)_2Cl] \cdot 1/2C_6H_6$. Reproduced with permission from ref. 119.

The compound $Au(PPh_3)_2Cl \cdot 1/2C_6H_6$ contains a central AuP_2Cl unit with planar, three-coordination at gold (Fig. 12) [119]. Bond distances are: Au—P = 2.323, 2.339 and Au—Cl = 2.500 Å; bond angles are: P—Au—Cl = 109.2, 118.7 and P—Au—P = 132.1°. The angular distortions from regular trigonal-planar geometry are attributable to steric repulsions between the bulky triphenylphosphine ligands. Similar three-coordinate AuL_2X units may also be present in the compounds $Au(PPh_3)_2(SCN)$ and Au[*o*-phenylenebis(dimethylarsine)]I [120].

A 1 : 2 : 1 complex, Au(2-diphenylphosindoline)$_2$I, is monomeric in dichloromethane and a non-conductor in nitrobenzene, implying a three-coordinate structure in solution [121]. However, preliminary crystallographic data indicate the ionic formulation $[AuL_2]I$ in the crystalline state so the actual coordination for this complex is questionable at present.

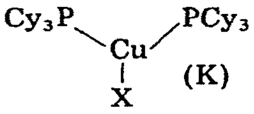
In contrast to the analogous Cu(I) and Ag(I) systems, NMR studies of $Au(PPh_3)_nCl$ solutions (n = 1—4) indicate no metal-anion bonding except for $Au(PPh_3)Cl$. The studies also suggest that $Au(PPh_3)_2Cl$ disproportionates with an equilibrium constant $\sim 10^{-1}$ at —80°C to give both three-coordinate and two-coordinate aurous—phosphine complexes (eqn. 29) [115]. The compound $[Au(bipy)(PPh_3)]PF_6$ was prepared from $(Ph_3P)AuCl$, 2,2′-bipyridyl, and $AgPF_6$ in dichloromethane solution [122a]. The coordination geometry is intermediate between trigonal planar and linear [122b]. The gold atom lies 0.10 Å out of the plane of the three coordinating atoms. The binding of the bidentate bipyridyl ligand is highly asymmetric, and the Au—P bond length is comparable to that in two-coordinate rather than three-coordinate Au(I) complexes. A remarkably similar coordination geometry was found in $[Hg(bipy)CH_3]^+$ [123]. Many other gold compounds have stoichiometries that nominally suggest three coordination. In most of these compounds, however, the metal achieves tetracoordination via oligomerization (e.g., AuX_3, R_2AuX, and $RAuX_2$; R = alkyl) or by solvation (e.g., AuR_3(solv)) [124].

$$Cl^- + 2Au(PPh_3)_2^+ \rightarrow [Au(PPh_3)_3]^+ + Au(PPh_3)Cl \qquad (29)$$

Analogous silver—phosphine complexes $Ag(PR_3)_2X$ (X = PF_6, BF_4, ClO_4), containing weakly coordinating anions, appear to be completely ionized in solution; hence, they are two-coordinate [115]. A series of $Ag(PR_2R')_2I$ complexes have been synthesized (R = Me, R′ = *p*-$NH_2C_6H_4$ or Ph; R = Et, R′ = *p*-$CF_3C_6H_4$), and several are reported to be monomeric (and hence three-coordinate) in solution [115]. However, a recent structural determination of $Ag(PPh_3)_2Br$ showed that it is dimeric via bromide bridges in the crystal [125]. This type of structure is unknown for triphenylphosphine complexes of copper(I) halides, and the difference is ascribed to sterically unfavorable nonbonding repulsions between hydrogen atoms on the phenyl groups and bromine atoms in the case of the smaller copper atoms.

A large number of nominally three-coordinate cuprous complexes of stoichiometry $Cu(PR_3)_2X$ have been prepared with pseudohalide ligands (X = Cl, Br, I, CN, SCN, N_3, NO_3, SPh, OPh, BH_4, and B_3H_6) [116,126]. A more limited series of 1 : 2 : 1 complexes has been prepared with the ligands diphenylphosphine [127a], triphenylstibine [127b], and 2-diphenylphosphindoline [121]. The ligands tris(*m*-tolyl)phosphine, methyldiphenylphosphine, dimethylphenylphosphine, ethyldiphenylphosphine, and several bidentate phosphines yield pseudotetrahedral complexes of the type $Cu(PR_3)_2NO_3$ [116]. The CuP_2X complexes may be divided into three general categories, depending on the nature of the anions.

Monomeric, three-coordinate compounds are obtained for CuL_2X complexes with unidentate anions (X = Cl, Br, I). The structure of $Cu(PPh_3)_2Br$ is very similar to that of $Au(PPh_3)_2Cl$ (Fig. 12) [128]. The coordination geometry of $Cu(PPh_3)_2Br$ is a distorted trigonal plane with the copper atom lying within 0.04 Å of the P_2Br plane. Bond angles and distances at copper are: P—Cu—Br = 112.8, 121.0°, P—Cu—P = 126.0°, Cu—P = 2.263, 2.282 Å, and Cu—Br = 2.346 Å. As in $Au(PPh_3)_2Cl$ angular deviations from ideal trigonal-planar symmetry are due to steric repulsions between the bulky triphenylphosphine ligands. The complex AuL_2I, where L = 2-diphenylphosphindoline, is also monomeric and three-coordinate [121]. It is likely that $Cu(PPh_3)_2Cl$ and $Cu(PPh_3)_2I$ also possess monomeric three-coordinate structures. However, the complexes $Cu(AsPhMe_2)_2Cl$, CuL_2X (L = 2-diphenylphosphindoline), and $Cu(PPh_2H)_2X$ are dimeric in the solid state with a double halide bridge [118,119,127a]. The complex $Cu(PPh_2H)_2Cl$ is also dimeric in solution [127a]. The tricyclohexylphosphine complexes $Cu(PCy_3)_2X$ are monomeric, three-coordinate, and probably have trigonal-planar structures of type (K) [129].



(K)

A second structural type of CuL_2X complex is formed by anions that can function as bridging groups (e.g. X = N_3, NCS, CN). These are dimeric compounds containing pseudotetrahedral copper typified by the structure of $[Cu(PPh_3)_2(N_3)]_2$, (Fig. 13) [130]. $[Cu(PPh_3)_2(CN)]_2$ apparently dissociates to a monomer in dilute solutions.

A third type of $[CuL_2X]$ complex results from anions that function as bidentate ligands (e.g., X = NO_3, BH_4, B_3H_8); these are monomeric, pseudotetrahedral CuL_2X complexes with bidentate X groups [116,126a,131]. The reaction of arylcopper compounds with dinitrophenylmethane, $PhCH(NO_2)_2$, in the presence of triphenylphosphine yields a bis(triphenylphosphine)copper salt of dinitro-phenylmethane in its *aci*-nitro form [132]. The geometry around copper is similar to that in the nitrate complex $[Cu(PPh_3)_2(NO_3)]$ [131], with one of the two nitro groups being bonded to copper in a bidentate fashion. The complex $Cu(PPh_3)_2(B_3H_8)$ has a bidentate B_3H_8 group coordinated symmetrically to copper through two B—H bonds. In contrast to the

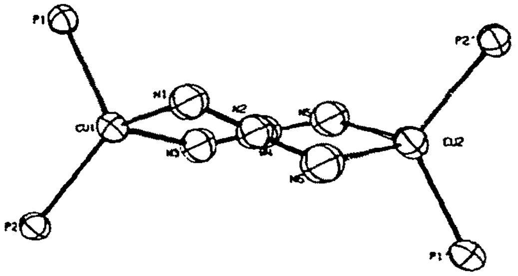
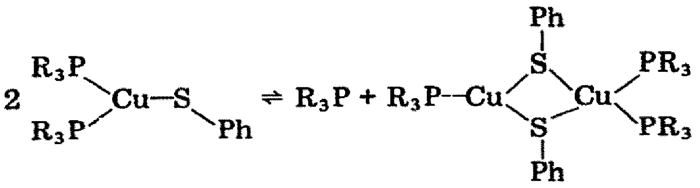


Fig. 13. A perspective of the structure of $[Cu(PPh_3)_2(N_3)]_2$. Reproduced with permission from ref. 130.

analogous silver complexes discussed above, excess PR_3 (R = *p*-tolyl) does not displace the borohydride anion in $Cu(PR_3)_2(B_3H_8)$ and $Cu(PR_3)_2(B_{10}H_{13})$, even in the presence of a large excess of phosphine [115].

Several authors have pointed out the remarkable structural similarity between $Cu(PPh_3)_2X$ complexes with monodentate and bidentate X groups [128,131—133]. If the center of the bidentate anion is considered to be a single coordination site, the bonding at the metal may be visualized as being three-coordinate. The Cu—P distances are comparable and even the orientations of the phenyl rings are very similar to those in discrete, three-coordinate CuL_2X complexes containing monodentate anionic ligands. From a comparison of the geometries of a large number of copper(I) complexes that contain the $(Ph_3P)_nCu$ grouping, Camus et al., [132] conclude that: (a) the Cu—P bond lengths in complexes of the same kind of phosphines (PPh_3, dpm, dpe) are dramatically influenced by the number of phosphine ligands bonded to the copper atom, whereas the Cu—P bond lengths are only slightly affected by the coordination number of the metal; (b) other secondary factors seem to affect the range of Cu—P bond lengths and the P—Cu—X bond angles. For the structural details and excellent discussions of this interesting aspect of the bonding and coordination number in CuL_2X compounds, see Davis et al. [128], Camus et al. [132] and Lippard et al. [133].

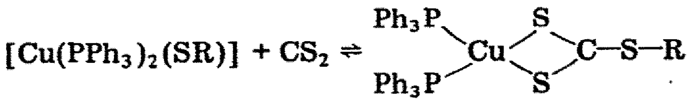
Reichle [126b] reported an interesting series of ML_2X copper(I) thiophenoxide and phenoxide complexes containing phosphine, arsine, and stibine ligands. In general, these complexes can be prepared readily by direct combination of cuprous halides and phosphine (or arsine or stibine) ligand in chloroform solution, followed by addition of the appropriate anion. Many of these complexes lose one or more phosphine ligands during sublimation or recrystallization to give oligomers containing an equal or higher coordination number at the metal. Reichle's molecular weight and stoichiometry data indicate three-coordinate copper(I) for the monomers $Cu(PPh_3)_2(OPh)$, $Cu(PPh_3)_2(SPh)$, and $Cu(PPh_3)(py)Cl$ and also for the dimers $[Cu(PPh_3)(OPh)]_2$, $[Cu(PPh_3)(SPh)]_2$, and $[Cu(PPh_3)_2]_2SO_4$ [126b]. However, owing to the known lability of copper(I)—phosphine and arsine systems, molecular weight data on solutions must be interpreted with caution. For example, the monomeric molecular weight observed for $Cu(PPh_3)_2(SPh)$ could arise either from a monomeric, three-coordinate species, or from dissociation of a phosphine ligand and formation of the dimeric complex $Cu_2(PPh_3)_3(SPh)_2$ (eqn. 30).



(30)

Formation of a dinuclear species in solution is quite possible considering the well-known stability of the dimeric $Cu_2L_3X_2$ compounds.

Certain 1 : 2 : 1 pseudohalide complexes, especially the triphenylphosphine complexes of sulfur or oxygen-containing anions (anion = SPh, OPh, O_2CCH_3, acac), react with carbon disulfide. The colorless phenoxide and thiophenoxide complexes, for example, reversibly bind carbon disulfide to give bright yellow "adducts" which revert to the original materials on heating to 90—100°C at atmospheric pressure, or to 70°C under vacuum. Crystal structure analyses on the CS_2 adducts of $Cu(PPh_3)_2SPh$ and $Cu(PPh_3)_2SEt$ showed that insertion into the Cu—SR bonds occurred instead of simple adduct formation [134,135]. The resultant complexes contain a copper atom with a distorted tetrahedral geometry, surrounded by two triphenylphosphine ligands and a bidentate trithiocarbonate ligand (eqn. 31).



(31)

The analogous silver complex, $Ag(PPh_3)_2(SPh)$, undergoes a similar reversible interaction with CS_2 [134].

Dines [136] reported a series of trifluoroacetate complexes $Cu(PR_3)_n$-(CF_3CO_2) (n = 1, 2, or 3) and one of these, $Cu(PPh_3)_2(CF_3CO_2)$, is nominally three-coordinate. However the trifluoroacetate group probably functions as a bidentate ligand in this complex, making copper four-coordinated.

The complexes ML_2X (where M = Cu or Ag, X = N_3 or NCS, and L is one of the monodentate phosphines PPh_3, PPh_2Me, PPh_2(*o*-tolyl), Ph_2POMe, or Ph_2POEt) have been studied extensively by Dori and co-workers [137—139]. Only 1 : 2 : 1 complexes were obtained with azide and thiocyanate ions, whereas the halide complexes give several different M : L : X ratios, e.g., 1 : 1 : 1, 1 : 1.5 : 1, 1 : 2 : 1, 1 : 3 : 1, and 1 : 4 : 1. With the exception of the PPh_2OR complexes, which decompose rapidly, the azide complexes are very stable, non-explosive materials. The stability of these copper azide complexes illustrates the stabilizing effect of phosphine ligands on metal azide linkages, which are often unstable. Dimeric $[ML_2X]_2$ structures are proposed for all of these solid azide and thiocyanate compounds on the basis of the known structures of the compounds $[Cu(PPh_3)_2(N_3)]_2$, $[Ag(PPh_3)_2(NCS)]_2$, and $[Cu(PPh_2Me)_2(NCS)]_2$ [129,138]. The complexes apparently dissociate in benzene and chloroform solutions, and give molecular weights corresponding to monomers. Again, we should note that molecular weight data alone are insufficient to rule out a neutral ligand dissociation from the dimeric complex, which would give a 1 : 1 mixture of free ligand and a dinuclear species as in eqn. (30) and an apparent monomeric molecular weight.

Several mercury(II) complexes that have a nominal three-coordinate composition $Hg(PR_3)X_2$ have been reported [140—142]. In most cases, however, the species are halide-bridged dimers involving pseudotetrahedral metals.

$M_2L_3X_2$ complexes. By a stoichiometric combination of CuX and L or by recrystallization of certain CuL_2X complexes, an interesting series of 2 : 3 : 2 complexes $Cu_2(PR_3)_3X_2$ (X = Cl, Br, I; PR_3 = PPh_3) may be isolated [143—145]. The $Cu_2L_3X_2$ formulations have also been obtained with L = $AsPh_3$ (X = Cl, I), with L = $SbPh_3$ (X = Cl, Br) [127], and with L = PPh_2H (X = Cl) [126]. The arsine and stibine compounds, however, dissociate in chloroform; thus the coordination number is questionable in these cases.

Molecular weight studies on the 2 : 3 : 2 complexes indicate a dimeric structure with little or no dissociation in solution. X-ray diffraction studies on the chloride compound (two crystal modifications) [146] and the iodide compound [147] confirm a dinuclear structure in the solid state (Fig. 14). A double halide bridge connects the two copper atoms, one copper atom has a distorted tetrahedral coordination from two halides and two phosphines, and the other metal achieves approximately trigonal-planar coordination via two halides and a phosphine. The latter copper atom lies in the plane of the two halides and the phosphine ligand. In the $Cu_2X_2(PPh_3)_3$ structures the Cu—P and Cu—X bond lengths are significantly shorter for the three-coordinate metal atom (ca. 0.15 Å shorter for Cu—X, and 0.05 Å

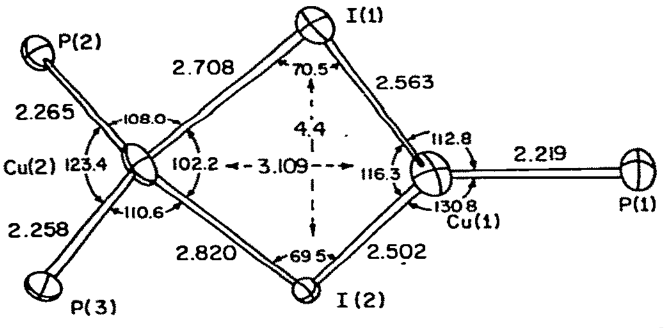
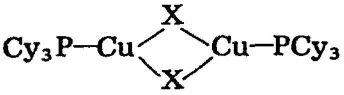


Fig. 14. A perspective of the structure of $Cu_2(PPh_3)_3I_2$. See ref. 134.

shorter for Cu—P), which can be attributed to the different covalent radii and steric repulsions for the three- and four-coordinate copper atoms.

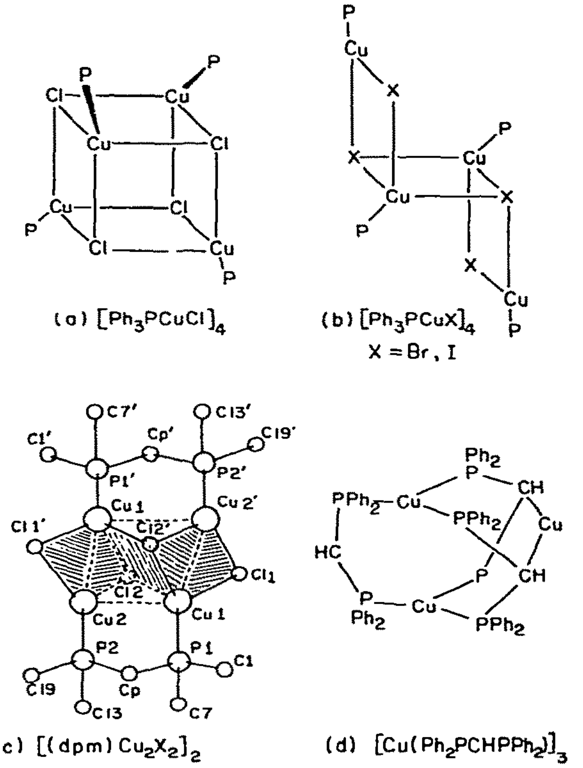
Most of the $(CuX)_nL_m$ systems, where $m > n$ and L is a monodentate phosphine or arsine ligand, are labile [115,127a,131,149]. For example, dichloromethane—toluene solutions of CuX in the presence of excess phosphine at —100°C contain predominantly $[CuL_2X]_2$, but when the temperature is raised above —70°C increasing amounts of CuL_3X, $Cu_2L_3X_2$, and monomeric CuL_2X are formed. As in the $Ni(PR_3)_n$ systems discussed above, complexes of the more bulky phosphines show increased dissociation of the phosphine ligands. In chloroform solutions with L : Cu ratios greater than 3 : 1, the principal species is CuL_3X (X = Cl, Br, I; L = PPh_2Me), whereas $Cu_2(PPh_3)_3X_2$ is the principal species with PPh_3 : Cu ratios between 2 : 1 and 3 : 1.

MLX complexes. A number of 1 : 1 : 1 CuLX complexes have been prepared with tertiary phosphine and arsine ligands. The compounds are generally tetramers with halide bridges and either a "cubane-like" (L = PPh_3, X = Cl; L = PEt_3, X = I; L = $AsEt_3$, X = I) or a "step-like", (L = PPh_3, X = Br, I) tetrameric architecture is found [127b,148—152]. The structures of the $[(Ph_3P)CuX]_4$(X = Cl, Br, I) series are particularly interesting and show how small variations in the ligands can change the structure dramatically. The chloride compound has a "cubane" structure (Fig. 15a) [150], whereas the bromide and iodide compounds form the "step-like" structure (Fig. 15b) [151,152]. Note that two of the four copper atoms in the "step-like" structures have trigonal-planar coordination. The bulkier ligand PPh_2Cy (Cy = cyclohexyl) forms a complex of composition $(Cu(PPh_2Cy)Br$, which is dimeric with bridging bromides, presumably containing three-coordinate copper. A nearly symmetric pentahaptocyclopentadienyl group is observed in complexes of the type $Cu(C_5H_5)PR_3$ [153]. The potentially three-coordinate complexes $CuX(CH_2{=}CHCH_2CH_2PEt_2)$ (X = Cl, I) and $CuCl(CH_2CHCH_2CH_2PCy_2)$ (Cy = cyclohexyl) are tetrameric and dimeric, respectively, each containing only four-coordinate copper atoms. Infrared spectra of the compounds $Cu(PCy_3)X$ (X = Cl, Br, I) have been interpreted in terms of three-coordinate, halide-bridged dimers (L) [129].



(L)

The $[Cu(L)X]_4$ tetramers react with various bases to give discrete three-coordinate, mixed-ligand complexes. Thus, monomeric CuLL′X complexes have been reported with L′ ligands such as pyridine, β-picoline and γ-picoline [154]. Similar compounds, $Cu(AsPh_3)LX$ (X = Br, I; L = α-, β-, γ-picoline, pyridine, quinoline, and isoquinoline), $Cu(PPh_3)LX$ (X = Ph, Br, I; L = β or γ-pico-



(a) $[Ph_3PCuCl]_4$

(b) $[Ph_3PCuX]_4$
X = Br, I

(c) $[(dpm)Cu_2X_2]_2$
X = Cl, Br, I

(d) $[Cu(Ph_2PCHPPh_2)]_3$

Fig. 15. Drawings that show: (a) the "cubane-like" structure of the tetramer $[CuCl(PPh_3)]_4$; (b) the "step-like" structures of the tetramers $[CuX(PPh_3)]_4$ (X = Br, I); (c) the "step-like" structure of the bis(diphosphine)-tetracopper complexes of $Ph_2PCH_2PPh_2$(dpm); and (d) the structure of the tricopper complex of the anion of dpm.

line, pyridine), and $Cu(SbPh_3)$(pyridine)I are monomeric in chloroform [127b].

$$[CuLX]_4 + 4L' \rightarrow 4[CuLL'X] \qquad (32)$$

Bidentate nitrogen ligands generally form tetracoordinate complexes of the type CuLX(bidentate).

The 1 : 1 : 1 complexes of silver(I) halides with 2-diphenylphosphindoline, AgLX, are dimeric and evidently three-coordinate [121]. The analogous gold(I) compounds are unassociated and two-coordinate.

Miscellaneous complexes. Copper(I) halides react with diphosphine ligands such as $Ph_2PCH_2PPh_2$ (dpm) and $Ph_2PCH_2CH_2PPh_2$ (dpe) to give compounds of several different stoichiometries $(CuX)_n$(diphosphine)$_m$ [155a]. Several dpm complexes contain trigonal-planar, three-coordinate copper(I) [155—160]. All of the $(CuX)_2$(dmp) complexes have a $(CuX)_4$ core that has a stepped geometry (Fig. 15c) in which two copper atoms are surrounded trigonally by two halides and one phosphorus atom from the bidentate, non-chelating ligand [155b,157,159]. The other two copper atoms are surrounded by three halides and one phosphorus atom in a pseudotetrahedral fashion. A related structure is also formed by the trimeric compound [CuCl-(dpm)]$_3$; in the latter case, however, the compound has the ionic formulation [Cu_3Cl_2(dpm)$_3$]Cl and involves only pseudotetrahedral copper [158a]. The Cu—P and Cu—X bond distances in several different types of copper(I)—phosphine structures are given in Table 10.

Treatment of arylcopper(I) compounds with $Ph_2PCH_2PPh_2$ (dpm) produces the parent aryl hydrocarbon and a molecular copper complex of

TABLE 10

Copper—phosphorus bond lengths, donor atoms, and coordination numbers for copper in some tertiary phosphine—copper(I)—complexes

Complex	Cu—P Å	$\Delta_{4,3}$*	Donor atoms	C.N. **	Ref.
$(Ph_3P)_2CuBr$	2.282(2)		BrP_2	3	128
	2.263(2)		BrP_2	3	
$(Ph_3P)_4Cu_4Cl_4$	2.193(2)		Cl_3P	4	150
	2.192(2)			4	
$(Ph_3P)_4Cu_4Br_4$	2.207(3)	0.013	Br_3P	4	151
	2.194(4)		Br_2P	3	
$(Ph_3P)_4Cu_4I_4$	2.242(4)	0.014	I_3P	4	152
	2.228(5)		I_2P	3	
$(Ph_3P)_3Cu_2Cl_2$	2.236(5)	0.057 ***	Cl_2P_2	4	147
	2.245(5)		Cl_2P_2	4	
	2.183(4)		Cl_2P	3	
$(Ph_3P)_3Cu_2I_2$	2.265	0.043 ***	I_2P_2	4	134
	2.258		I_2P_2	4	
	2.219		I_2P	3	
$(dpm)_2Cu_4Cl_4$	2.197(5)	0.002	Cl_3P	4	159
	2.195(4)		Cl_2P	3	
$(dpm)_2Cu_4Cl_4$	2.203(3)	0.018	Cl_3P	4	
	2.185(3)		Cl_2P	3	
$(dpm)_2Cu_4Br_4$	2.19(1)	0.010	Br_3P	4	155, 157
	2.18(1)		Br_2P	3	
$(dpm)_2Cu_4I_4$	2.230(8)	0.012	I_3P	4	155, 157
	2.218(8)		I_2P	3	

* Difference (Å) between two chemically equivalent bond lengths, which reflect the different coordination numbers of the two different copper atoms.

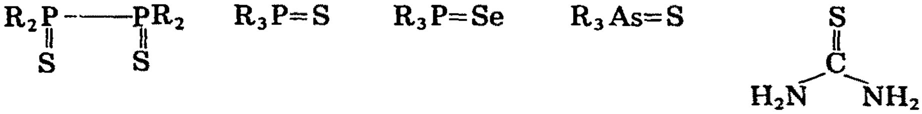
** Coordination number of the copper atom.

*** Difference obtained by taking the mean value of the two Cu—P distances for the four-coordinate copper.

deprotonated dpm [160]. The compound is trimeric with the copper atoms arranged at the vertices of a nearly regular isosceles triangle. The two basal copper atoms have a nearly trigonal-planar geometry and are bridged by three non-chelating ligand molecules (av. Cu—P distance = 2.317(5) Å) [160]. The third copper atom is rather unusual, as it bridges the methine carbon atoms of the two ligand molecules at an angle of 158.0(8)° and has Cu—C bond lengths of 1.96(2) and 2.00(2) Å (Fig. 15d). Thus, the aryl—copper reagent abstracted a proton from the central methylene group and produced an anionic diphosphine ligand, i.e., $Ph_2P\text{---}CH\text{---}PPh_2^-$, and the complex can be viewed as $[Cu(I)(Ph_2P\text{---}CH\text{---}PPh_2)]_3$.

(b) Phosphine sulfides, phosphine selenides, and arsine sulfide complexes

Ligands belonging in this category all possess the general structure R_3YZ where Y = P, or As, and Z = S or Se. The only known means of coordination for these ligands is through the Z atom, either as a terminal or as a



$R_2P(=S)\text{—}P(=S)R_2$ $\quad R_3P{=}S \quad R_3P{=}Se \quad R_3As{=}S \quad (H_2N)_2C{=}S$

phosphine sulfides

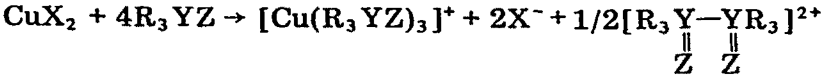
phosphine selenides

arsine sulfides

thiourea(tu)

bridging ligand. Until recently these compounds were generally believed to be poor donor ligands [161,162]. In the past few years, however, a rather extensive coordination chemistry of these ligands has been developed with the "class b" metals Pd(II), Pt(II), Ag(I), Cd(II), and Hg(II) [163—180]. Pseudo-tetrahedral ML_2X_2 complexes of tertiary arsine and phosphine sulfide ligands have been synthesized also with first row transition metal ions such as cobalt(II), nickel(II), and Cu(I) [168—170], but these are not discussed further as they are not pertinent to the three-coordination theme of this review.

Sulfides and selenides. Solutions containing phosphine sulfides, phosphine selenides, and arsine sulfides reduce copper(II) salts [166,172,178—180] to form copper(I)—R_3YZ complexes having a 1 : 1 or 1 : 3 stoichiometry depending on the anion, the particular R_3YZ compound, and the M : R_3YZ mole ratio used (eqns. 33 and 34).

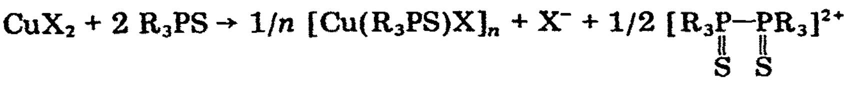


$$CuX_2 + 4R_3YZ \rightarrow [Cu(R_3YZ)_3]^+ + 2X^- + 1/2[R_3\underset{Z}{\underset{\|}{Y}}\text{—}\underset{Z}{\underset{\|}{Y}}R_3]^{2+} \qquad (33)$$

$(X = BF_4, ClO_4, NO_3)$

$(R_3YZ = R_3PS$, R = Me, Et, i-Pr, Me_2N, Ph; Ph_3PSe; Ph_3AsS; or $PhMe_2PS)$

With excess LiX:



$$CuX_2 + 2\ R_3PS \rightarrow 1/n\ [Cu(R_3PS)X]_n + X^- + 1/2\ [\underset{\overset{\|}{S}}{R_3P}-\underset{\overset{\|}{S}}{PR_3}]^{2+} \qquad (34)$$

(X = Cl, Br, I, SCN)

Although either copper(I) or copper(II) salts may be used in these syntheses, preparations with copper(II) salts are somewhat less satisfactory since the chalcogen sulfide or selenide must also serve as the reducing agent and be partially consumed during the reaction [170].

Nicpon [166] first prepared and characterized the 1 : 3 Cu : L complex $[Cu(SPMe_3)_3]ClO_4$ in 1965. Elemental analyses, infrared spectra, and conductance values on the complex indicated the presence of a three-coordinate copper cation. A crystal structure determination in 1970 confirmed that it was an authentic three-coordinate transition metal cation. In addition to showing that the 3 : 1 complexes of tertiary phosphine sulfides contained three-coordinate cations, the structure was the first of a coordinated tertiary phosphine sulfide (Fig. 16) [174, 175]. The structure contains a planar CuS_3 unit, which closely approximates trigonal symmetry. The Cu—S distances

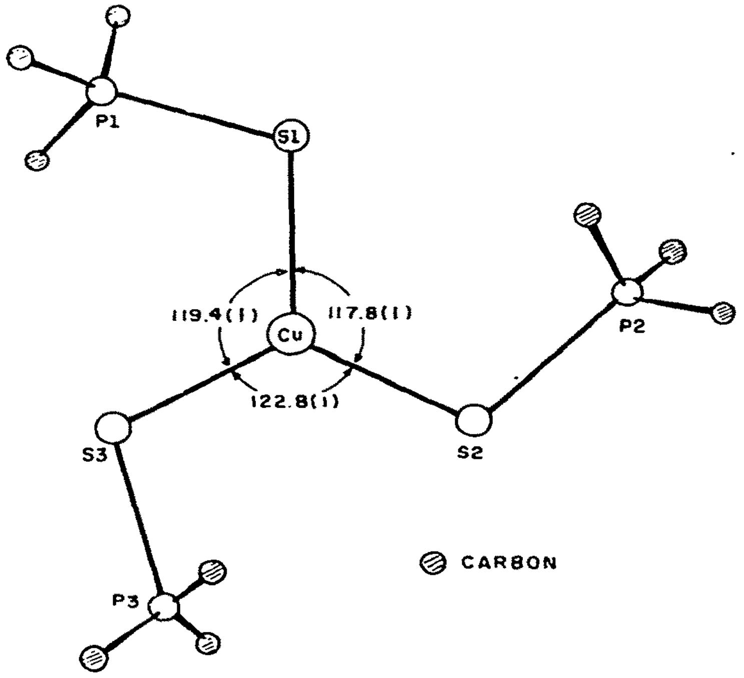


Fig. 16. A perspective drawing of the three-coordinate cation $[Cu(SPMe_3)_3]^+$. Reproduced with permission from ref. 174.

range from 2.248 to 2.264 Å and the S—Cu—S angles are in the range 117.8 to 122.8°. The nearest axial contact to copper is 6.2 Å to a copper atom in an adjacent unit cell. The salts $[Cu(SPMe_3)_3]BF_4$ and $[Cu(SPMe_3)_3]ClO_4$ are isomorphous, as are the analogous triphenylphosphine sulfide salts.

In general, the 3 : 1 phosphine sulfide complexes are air stable, crystalline compounds which are uni-univalent electrolytes in nitromethane. The nitrate compound $[Cu(SPMe_3)_3]NO_3$, is less stable in solution than the tetrafluoroborate and perchlorate salts, although the conductivity values in nitromethane are appropriate for uni-univalent electrolytes, i.e., three-coordinate $[Cu(SPMe_3)_3]^+$ cations in solution. Also, the infrared spectrum of $[Cu(SPMe_3)_3]NO_3$ is consistent with an ionic nitrate group [177,180].

Proton NMR and solution infrared studies indicate that the $[CuL_3]^+$ complexes (L = Ph_3PSe, Ph_3AsS, Ph_3PS, Me_3PS, Et_3PS, $(iPr)_3PS$, $(Me_2N)_3PS$, and $PhMe_2PS$) undergo varying degrees of dissociation and exchange in nonaqueous solutions. For $[Cu(SPMe_3)_3]BF_4$ and other trialkylphosphine sulfide complexes, ligand exchange between the three-coordinate cation and excess ligand occurs at ambient temperatures [180]. About 75% of one ligand is dissociated from the $[Cu(SPPh_3)_3]^+$ cation in a 10^{-2} M acetone solution. Equilibrium constants for the dissociation reaction are $27 \cdot 10^{-3}$, $1.2 \cdot 10^{-3}$, and $<0.1 \cdot 10^{-3}$ for L = $SPPh_3$, $SPPhMe_2$, and $SPMe_3$, respectively. These

$$[CuL_3]^+ \overset{K_{diss}}{\rightleftharpoons} [CuL_2]^+ + L \tag{35}$$

values could reflect either the decreasing steric requirements or the increasing polarity and basicity of the ligands as the bulky phenyl groups are replaced by methyl groups. An infrared and Raman study of Cu—S vibrations supports a correlation between the dissociation trends and the basicity of the sulfur atom in the R_3PS ligands [176].

Although the $[CuL_3]^+$ cations do not form significant concentrations of pseudotetrahedral $[CuL_4]^+$ species in the presence of excess ligand, they do react with halide and pseudohalide ions (X = Cl, Br, I, SCN) to give polynuclear $[CuLX]_n$ compounds that are relatively insoluble in common organic solvents [165,177,178]. Coordinating solvents such as DMF cause decomposition of the compounds. A structure determination of $Cu(SPMe_3)Cl$ revealed a trimer containing a six-membered Cu_3S_3 ring with an approximate chair conformation, the PMe_3 groups occupying positions equatorial to the ring and chloride ions occupying positions between the axial and equatorial locations (Fig. 17) [178,179]. Each trimethylphosphine sulfide ligand bridges two copper atoms symmetrically, the two independent Cu—S distances being 2.264 and 2.266 Å. The coordination environment around copper is a distorted trigonal plane; in addition the structure contains terminally-bound chloride ligands (Cu—Cl = 2.209, 2.223 Å). Angles at copper are in the ranges 103.0—111.7° (S—Cu—S) and 123.8—125.2° (S—Cu—Cl).

The compounds $[Cu(SPMe_3)X]_3$ (X = Br or I) have properties similar to the cyclic trimer $[Cu(SPMe_3)Cl]_3$ described above. The P—S stretching fre-

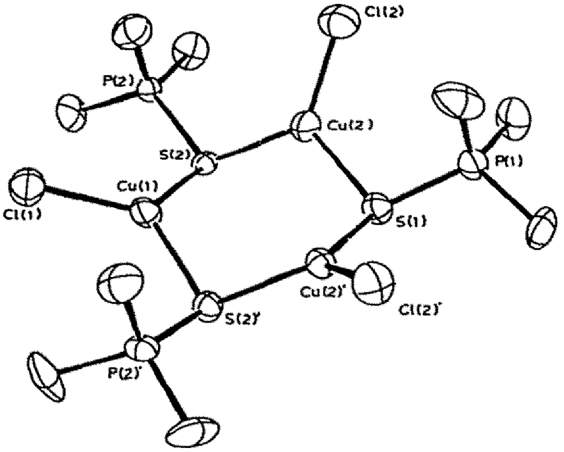


Fig. 17. A perspective drawing of [CuCl(SPMe$_3$)]$_3$. The primed atoms designate those related by the crystallographic mirror plane. Reproduced with permission from ref. 179.

quency in each of these compounds is decreased ca. 40 cm^{-1} from the value of the free ligand, indicative of bridging phosphine sulfide groups. Different structural types, however, are formed by Cu(SPPh$_3$)Cl and Cu(SPMe$_3$)(SCN). The ν_{PS} in these compounds is decreased ca. 24 to 35 cm^{-1} as in [Cu(SPMe$_3$)$_3$]ClO$_4$, indicating terminally bonded phosphine sulfide groups. A structure determination of Cu(SPMe$_3$)(SCN) has confirmed this prediction. The latter complex contains an infinite chain with bridging thiocyanate groups, terminally bonded SPMe$_3$ ligands, and three-coordinate copper atoms [181]. However, one must use caution in assigning structures solely on the basis of infrared spectra. For example, all the compounds Cu(SPMe$_3$)X (X = Cl, Br, I) have comparable solubility properties and infrared spectra, yet preliminary X-ray data for the isomorphous bromide and iodide derivatives exclude a cyclic trimer, as was observed for [Cu(SPMe$_3$)Cl]$_3$.

Interesting changes in ligand geometry, coordination geometry, and ν_{PS} in various complexes and derivatives of trimethylphosphine sulfide can be noted in Table 11. The only structural parameter in the Me$_3$PS ligand that changes significantly when the sulfur atom is bonded to one copper atom, to two copper atoms, or to one methyl group, is the P—S distance. Increasing the covalent nature of the atom bonded to sulfur produces a slight increase in the P—S distance (1.96 to 2.05 Å) and a decrease in the P—S stretching frequency (565 to 502 cm^{-1}). These observations, along with the fact that the P—S—X angle is nearly tetrahedral (103.9—110.1) in each case, suggests that the sulfur hybridization is essentially *sp*^{3} in all the Me$_3$PS derivatives and that little or no S—P multiple bonding occurs in these compounds [164].

Although the complex Hg(Ph$_3$PSe)I$_2$ is nominally three coordinate, its poor solubility properties suggest a polymeric nature and a higher coordination number [165,166]. King and McQuillan [164] and Dalziel et al., [165]

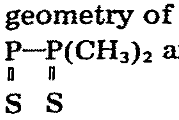
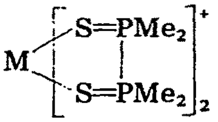
TABLE 11

Structural and vibrational properties of trimethylphosphine sulfide derivatives

Compound	M—S bond distance	P—S bond distance (Å)	P—S—X angle (deg)	ν_{P-S} (cm^{-1})	Reference
Me_3PS	—	1.959(2)	—	565	175
$[Cu(Me_3PS)_3]ClO_4$	2.253—2.264	1.982—2.001(4)	104.6(2)—110.1(2)	540	174,175
$[Cu(Me_3PS)Cl]_3$	2.264—2.267	2.025(2)	103.88(6)—104.72(5)	520	178,179
$[Me_3PSCH_3]I$	—	2.05(1)		502	179,181

have also reported a series of $HgLX_2$ complexes (L = Ph_3PSe, Ph_3AsS, or Ph_3PS, and X = Cl, Br, or I). X-ray powder patterns show $Hg(Ph_3PS)Cl_2$, $Hg(Ph_3PSe)Cl_2$, and $Hg(Ph_3AsS)Cl_2$ to be isomorphous with each other but not with $Hg(Ph_3AsO)Cl_2$, which has a dimeric, oxygen-bridged structure [182,183]. The former compounds have ν_{PS} and ν_{P-Se} in the ranges 590—592 cm^{-1} and 542—543 cm^{-1}, respectively, which would indicate terminally bound Ph_3YZ ligands. It is probable that all of these $HgLX_2$ complexes involve pseudotetrahedral metal coordination and halide bridges.

The bulky ligand tris(dimethylamino)phosphine sulfide forms pseudotetrahedral CuL_4^+ cations [170] when it is used in large excess. The silver(I) complex $AgL(NO_3)$ is a low conductor in nitromethane and its infrared spectrum indicates a coordinated nitrate group. However, the infrared spectrum does not distinguish between a monodentate or bidentate nitrate group, and either a two-coordinate or a three-coordinate complex is possible. The mercury(II) complex $HgLBr_2$ is a non-electrolyte in nitromethane and its ν_{PS} indicates a terminally bonded phosphine sulfide group. Either a dimeric, pseudotetrahedral structure or a monomeric, three-coordinate structure would be consistent with these data.

Since a large number of three-coordinate copper(I) complexes have been prepared from monodentate R_3PS, R_3PSe and R_3AsS ligands [163—172], it was of interest to determine the actual coordination number and geometry of complexes containing the potentially bidentate ligand  $(CH_3)_2\underset{\underset{S}{\|}}{P}—\underset{\underset{S}{\|}}{P}(CH_3)_2$ and its tetraethyl analog. The perchlorate and tetrafluoroborate copper(I) complexes contain two ligand molecules, are uni-univalent electrolytes, and have been formulated as four-coordinate,  cations [163,166]. A structure determination of $[Cu(Me_2P(S)P(S)Me_2)_2]ClO_4$ subsequently confirmed a pseudotetrahedral structure around Cu and the chelating nature of the diphosphine disulfide ligand [181]. The nominally three-coordinate complex $CuCl(Me_4P_2S_2)$ [166] was recently shown to be a molecular, dinuclear compound in which the $Me_4P_2S_2$ ligand is chelated and each Cu(I) is surrounded by a tetrahedral array of three sulfur atoms and one chlorine atom [184].

(c) Thiourea complexes

A series of synthetic and structural studies by Amma and co-workers on copper(I) and silver(I) complexes of thiourea (tu) has revealed a fascinating and intricate coordination chemistry that often involves three-coordinate metal atoms. Compounds having quite different stoichiometries and structures are formed with only subtle changes in reaction conditions; sometimes several products are isolated from one reaction mixture.

The parent member of the [M(tu)$_n$]$^+$ series may be considered to be the [Cu(tu)$_4$]$^+$ cation, which has a nearly regular tetrahedral structure with Cu—S distances of 2.345(2) [185] and 2.139—2.362 Å [186] with chloride and hexafluorosilicate counterions, respectively. The Cu—S distances in the three-coordinate copper complexes of thiourea are generally ca. 0.1 Å shorter than in the [Cu(tu)$_4$]$^+$ cation [187]. A similar bond contraction was noted for the three-coordinate complexes in the M(PR$_3$)$_n$ series and discussed in Section III(a).

An isolated [M(tu)$_3$]$^{n+}$ unit, the structural prototype for the three-coordinate series of thiourea complexes, has not been observed by direct structural methods. The ionic complex Cu(tu)$_3$Cl is dinuclear with bridging thiourea groups and pseudotetrahedral copper atoms [188,189]. The 3 : 1 complexes [Cu(tu)$_3$]BF$_4$ and [Cu(*N,N'*-dimethylthiourea)$_3$]BF$_4$ are sulfur-bridged dimers with tetrahedral Cu(I) [187]. However, some substituted thioureas give trigonal-planar CuL$_3^+$ groups, as in the salts [Cu(tmtu)$_3$]BF$_4$ (Fig. 18) and [Cu(entu)$_3$]$_2$SO$_4$ (Fig. 19) (tmtu = tetramethylthiourea; entu = ethylene-

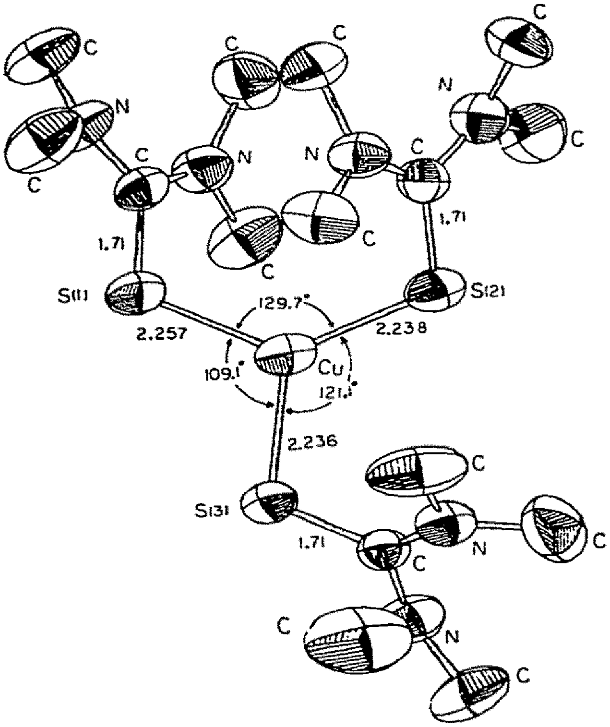


Fig. 18. The structure of [Cu(tmtu)$_3$]$^+$ showing the non-symmetrical arrangement of the tetramethylthiourea ligands around copper. Reproduced with permission from ref. 187.

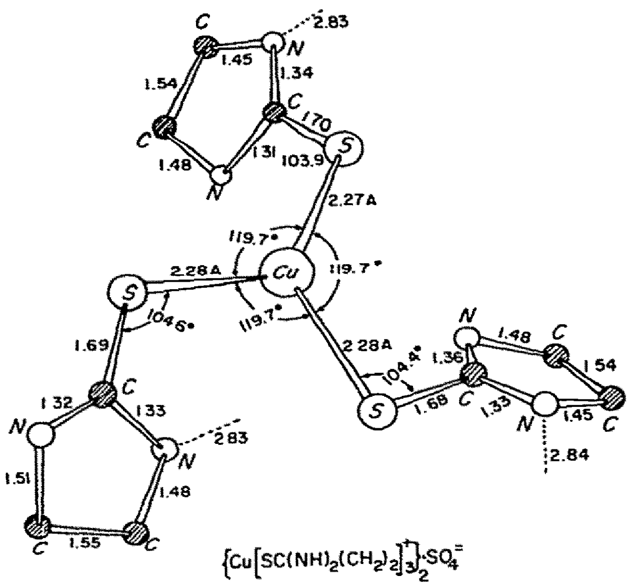


Fig. 19. The structure of the $[Cu(entu)_3]^+$ ion showing the arrangement of ligands. N—H ··· O hydrogen bonds are present between three nitrogen atoms and oxygen atoms of a sulfate group. There are two independent, essentially identical, ions per cell. Reproduced with permission from ref. 187.

thiourea) [187,188]. The CuS_3 unit has trigonal-planar geometry in $[Cu(entu)_3]^+$, with Cu—S distances in the range 2.27—2.28 Å and all three S—Cu—S angles being 119.7° (Fig. 19). The molecule has a propeller-like arrangement of ligands similar to that observed in $[Cu(SPMe_3)_3]^+$ [174]. The geometry of the $[Cu(tmtu)_3]^+$ion deviates somewhat more from a trigonal-planar arrangement, the Cu—S distances ranging from 2.257 to 2.238 Å and the S—Cu—S angles being 109.1, 121.1, and 129.7° (Fig. 18). Distortions of the CuS_3 unit from D_{3h} symmetry were attributed to steric interactions between adjacent tetramethylthiourea ligands.

The 1 : 2 complex, $CuCl(tu)_2$, has an infinite chain structure with ionic chlorides and thiourea ligands bridging three-coordinate copper atoms (Fig. 20) [190,191]. The crystallographic unit consists of two very similar $CuCl(tu)_2$ formula units. Both copper atoms lie approximately in the middle of a triangle of three sulfur atoms, two sulfur atoms coming from bridging thiourea groups, which form vertices of adjacent S_3 triangles (Cu—S = 2.23—2.31 Å), and one sulfur atom from a terminally bonded thiourea ligand (Cu—S = 2.23, 2.24 Å). The Cu—Cu separations alternate between short and long distances (2.98 and 4.31 Å) and each Cu is weakly bonded to a chloride ion in the axial position (Cu—Cl = 2.83, 3.16 Å). The two independent copper atoms lie 0.15 and 0.23 Å from their respective S_3 coordination planes. The relatively short Cu—S separations are attributed to substantial covalency in the metal—ligand bonding.

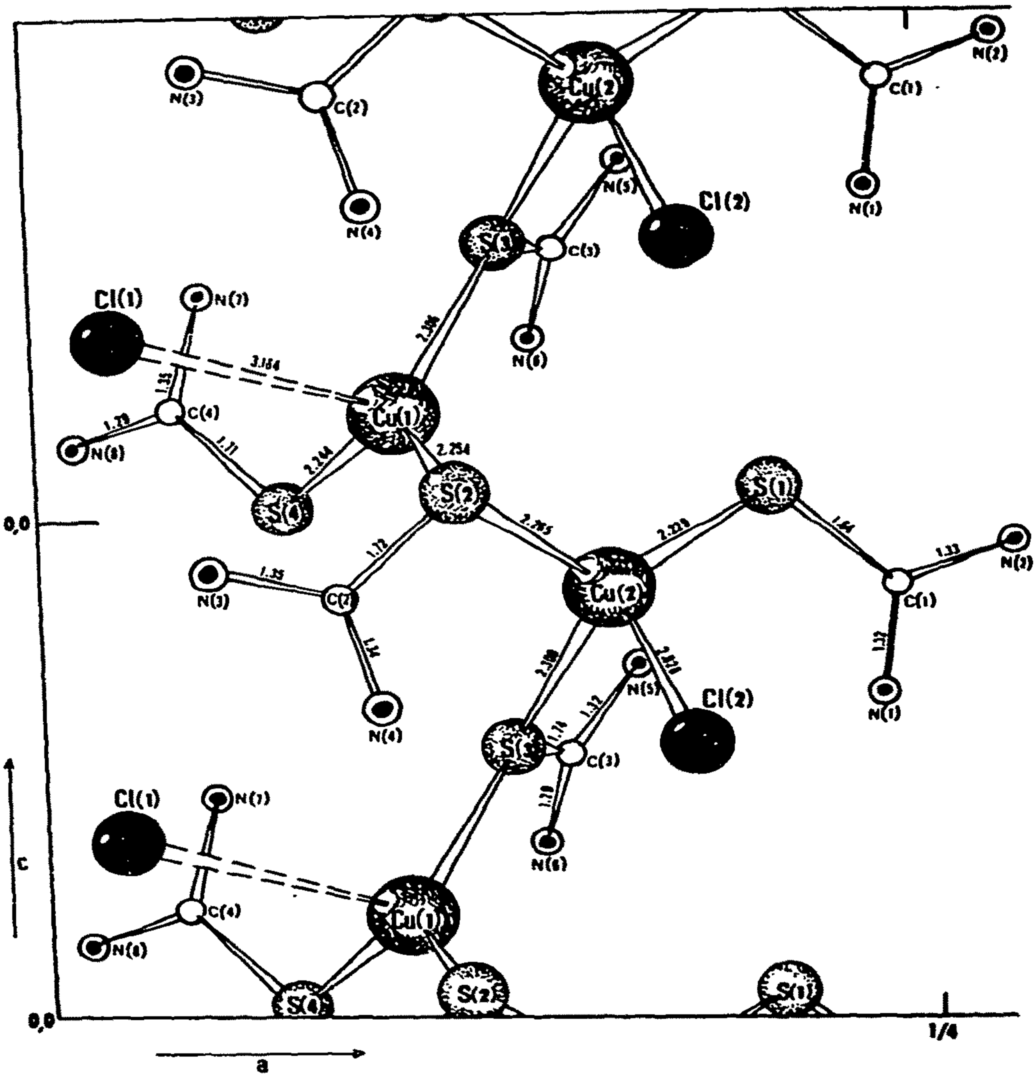


Fig. 20. A segment of the Cu—S—Cu chain in $CuCl(tu)_2$ viewed down the *b* axis. Cu(1) is the three-coordinate copper atom. Reproduced with permission from ref. 191.

One interesting feature of the $CuCl(tu)_2$ structure that is also observed in several other thiourea complexes is the presence of two distinct modes of sulfur bridging [191]. This type of bridging differs from that in the phosphine sulfide complexes, where terminal bonding and a nearly tetrahedral geometry at sulfur were observed in each case (Section IIIb). One bridging type has a thiourea approximately coplanar with the Cu—S—Cu′ plane, a Cu—S—Cu′ angle of ca. 135°, and a Cu—Cu′ distance of ca. 4.3 Å. The bonding may be interpreted in terms of two conventional electron-pair bonds

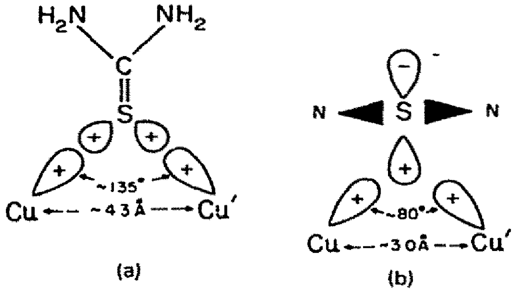


Fig. 21. Bonding pictures for the two types of thiourea sulfur bridging in copper—thiourea complexes; (a) has the CuS_2 and thiourea units coplanar; (b) has the Cu_2S and the thiourea units orthogonal.

between copper σ-type orbitals and the two filled sp^2 orbitals on the thiourea group (Fig. 21(a)). In the second type of S-bridging, the thiourea group is approximately orthogonal to the Cu—S—Cu′ plane, the Cu—S—Cu′ angle is ca. 80°, and the Cu—Cu distance is approximately 3.0 Å. In this case an electron-deficient three-center, two-electron bond involving appropriate σ-orbitals from each copper and a p_π(S—C) molecular orbital is proposed to account for the bonding (Fig. 21(b)). Alternatively, the bonding in the bridge may be viewed as being similar to that of ethylene, involving the C=S double bond. With the latter interpretation, the CuL_3 moiety would be even closer to planarity, but the S—Cu—S angles would distort more from 120°. It is proposed that the true bonding picture is intermediate between these two extremes, and that the maximum bonding density is displaced partially toward the carbon atom [191]. However, in neither case is the geometry of the thiourea ligand (including the C—S bond length) altered significantly from that observed in the free ligand, even though significant metal arrow ligand bonding involving the π(S—C) orbital should increase the S—C distance.

Several remarkably different complexes which have Cu : tu ratios between 1 : 2 and 1 : 3, have been studied. The salt $[Cu_4(tu)_{10}](SiF_6)_2 \cdot H_2O$ contains six-membered Cu_3S_3 rings [192] similar to those found in $[Cu(SPMe_3)Cl]_3$. Adjacent six-membered rings are connected by four-membered Cu_2S_2 rings to give an infinite chain structure. Each copper atom is surrounded by four sulfur atoms in a distorted tetrahedral arrangement, with Cu—S distances in the range 2.27—2.39 Å and S—Cu—S angles in the range 95—120°. The structure of $[Cu_4(tu)_9](NO_3)_4$, whose molecular formula contains one less thiourea ligand, shows a rectangular array of copper atoms connected by thiourea bridges [193,194]. Each copper is coordinated by four thiourea molecules in a pseudotetrahedral structure with Cu—S distances in the range 2.291—2.472 Å, and five distinctly different types of thiourea bonding are present. A similar rectangular array was found in the phosphine complex $[(CuI)_2(dpm)]_2$ that was discussed in Section IIIa (ii). The situation is even more complicated, as another salt, $[Cu_4(tu)_9](NO_3)_4$, has a completely

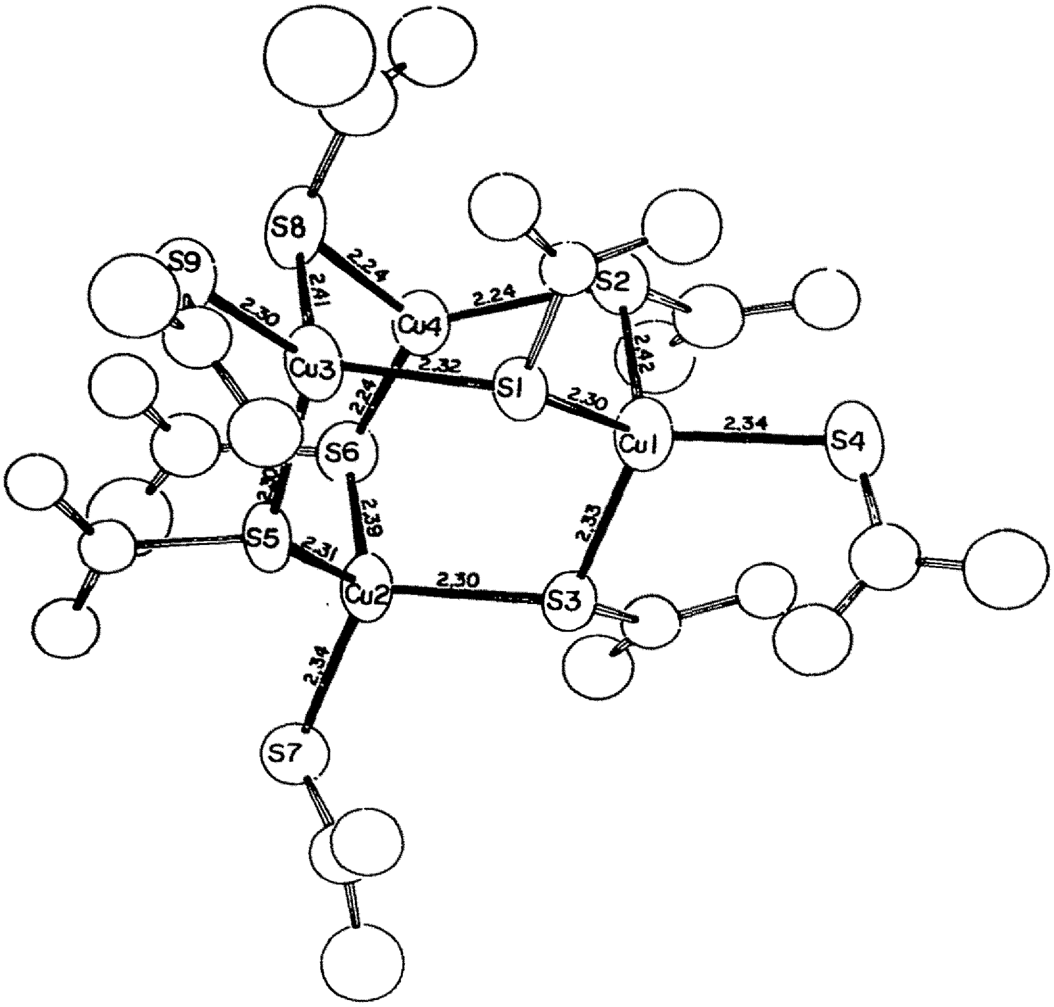


Fig. 22. A perspective drawing of the $[Cu_4(tu)_9]^{4+}$ cluster, which has an adamantine-like structure. Cu(4) is the trigonal-planar copper atom. Published with permission of E.L. Amma, ref. 194.

different structure that is based on a tetrahedron of copper atoms [194] (Fig. 22). Six thiourea ligands serve as bridging groups between the copper atoms, forming an adamantine-like framework. The remaining thiourea ligands are coordinated to three of the four copper atoms so that pseudotetrahedral and trigonal-planar copper ions are present in a 3 : 1 ratio. The compound $[Cu_4(tu)_6](NO_3)_4$ also has a molecular framework based on the adamantine structure; however in this case all the thiourea ligands are involved in bridges between copper atoms (Fig. 23) [194], and all four copper atoms are three-coordinate.

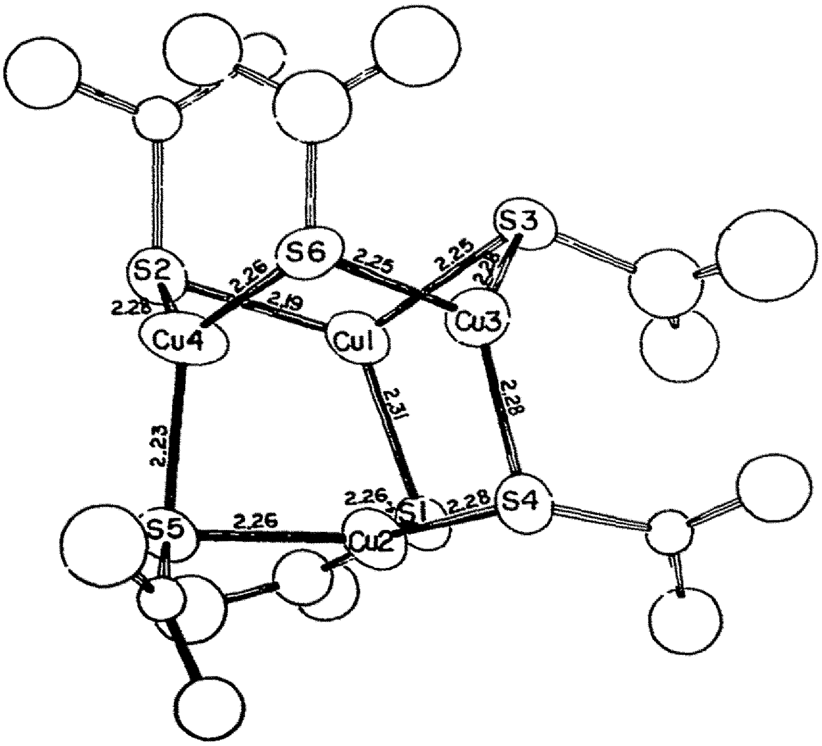


Fig. 23. A perspective drawing of the $[Cu_4(tu)_6]^{4+}$ cluster, which has an adamantine-like structure similar to that in $[Cu_4(tu)_9]^{4+}$. However, in the $[Cu_4(tu)_6]^{4+}$ cluster each copper atom is three-coordinate. Published with permission of E.L. Åmma, ref. 194.

Many other thiourea complexes have been prepared and probably involve three-coordinate complexes, although characterization data are scarce. Early work by Morgan and Burstall [195] with thiourea led to formulation of the copper complexes as: $Cu(tu)_2NO_3 \cdot H_2O$, $[Cu_2(tu)_5](NO_3)_2$ with one or two water molecules, $[Cu_3(tu)_7](NO_3)_3$, and $[Cu_5(tu)_{11}](NO_3)_5 \cdot 8H_2O$. With ethylenethiourea(entu) the following complexes were isolated: $[Cu(entu)_4]NO_3$, $[Cu_2(entu)_5 \cdot H_2O](NO_3)_2 \cdot 3H_2O$, $[Cu_2(entu)_5H_2O](NO_3)_2$, and $[Cu(entu)]_2O$. With silver and ethylenethiourea (entu) Morgan and Burstall isolated the following compounds, which have Ag : entu ratios of 1 : 4, 1 : 3, 1 : 2, 2 : 3 and 1 : 1 : $[Ag(entu)_4]NO_3$, $[Ag(entu)_3]NO_3$, $Ag(entu)_3Cl$, $Ag(entu)_2Br$, $[Ag_2(entu)_3]S_2O_8$, $Ag(entu)Cl$ and $[Ag(entu)]_2O$. Potentially three-coordinate gold and mercury complexes, $Au(entu)_2Cl \cdot H_2O$ and $[Hg(entu)_3](NO_3)_2$ were also isolated, along with the four-coordinate complexes $[Cd(entu)_4](NO_3)_2$, $[Pd(entu)_4](NO_3)_2$, $Cd(entu)_2X_2$, and $Pd(entu)_2X_2$.

Fyfe [196] determined the Ag^+—tu stability constants and demonstrated the probable existence of three-coordinate $Ag(tu)_3^+$ species in solutions. The structure of a $Ag(tu)_3^+$ complex, however, has not been determined to date. A 1 : 2 : 1 silver compound, $Ag(tu)_2Cl$, possesses a chain structure with bridging thiourea groups quite similar to that of $Cu(tu)_2Cl$ discussed above [197,198]. Two $Ag(tu)_2Cl$ formula units are present in the crystallographic asymmetric unit. The two silver atoms are separated from the chloride ions by 2.854 and 3.036 Å; both three- and four-coordinate silver atoms are present in this structure. As with $Cu(tu)_2Cl$, the M—M separations alternate between short (3.134 Å) and long (4.710 Å) distances, and both "in-plane" and "out-of-plane" thiourea bridges are present. The Ag—S distances, 2.48—2.59 Å, indicate relatively strong covalent bonding [198].

In contrast to the Cu(I) and Ag(I) cases discussed above, a recent structure determination of $AuCl(ethylenethiourea)_2$ has shown the coordination geometry around gold to be highly distorted from three-coordination toward a linear two-coordination [122].

Compounds of the type $Hg(tu)_2XY$ ($X = Cl, Br, I$ and $Y = BF_4, ClO_4, CF_3CO_2$) are reported to give either three-coordinate $[Hg(tu)_2X]^+$ or possibly dimeric, four-coordinate $[Hg(tu)_2X]_2^{2+}$ cations in solution [199]. A structure determination of $Hg(tu)_2Cl_2$ revealed discrete ions Cl^- and $[Hg(tu)_2Cl]^+$ in the crystal, the latter having a distorted trigonal-planar structure (C_{2v} symmetry) [200]. The bond distances and angles around mercury are: Hg—S = 2.37 Å, Hg—Cl = 2.56 Å, S—Hg—S = 128.7°, and S—Hg—Cl = 110.6°.

Marcotrigiano and Battsituzzi [201] reported that the nominally three-coordinate 1 : 1 complexes, $Hg(tmtu)X_2$ ($X = Cl, Br, I$), were dimeric in benzene; thus they were formulated as four-coordinate mercury complexes. However, in view of the crystal structure of $[Hg(tu)_2Cl]Cl$ [200], the tmtu complexes may be three-coordinate in other solvents or in the solid state.

(d) Halide and pseudohalide complexes

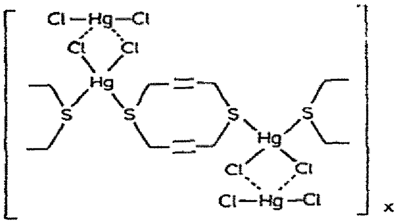
Many transition metal halides and pseudohalides of Groups IB and IIB have empirical formulas, MX_3^{n-}, suggesting three coordination. However, the number of MX_3^{n-} anions that actually attain this coordination number is small, since higher coordination numbers are often obtained by X-bridging (e.g., $[Hg(SCN)_3]_2^{2-}$, $[AuX_3]_2^{4-}$, $[CuCl_3]_2^{2-}$, $[PtCl_3]_2^{2-}$, $[HgI_3]_2^{2-}$, $[Ni(CN)_3]_2^{2-}$, etc.).

Halides. Most examples of well-characterized three-coordinate complexes of Group IB or Group IIB metals are with mercury(II). A structure determination of the salt $[SMe_3][HgI_3]$ revealed discrete, planar HgI_3^- ions with Hg—I distances of 2.65—2.71 Å and I—Hg—I angles in the range 112.8—123.6° [202]. The salt $[NMe_4][HgBr_3]$, on the other hand, contains distinctly pyramidal tribromomercurate ions [203]. The mercury atom lies 0.32 Å out of the Br_3 plane, the Hg—Br distances are 2.48—2.56 Å, and the Br—Hg—Br angles are 113.3—125.3°. The $HgBr_3^-$ ion is reported to be solvated to give four- or five-coordinate species in polar solvents.

All members of the series $[AMe_4][HgX_3]$ ($A = N$ or P; $X = Cl, Br,$ or I) are reported to be isomorphous [204]. Mixed halide anions such as HgI_2Br^- and

$HgCl_2I^-$ appear to have mononuclear, three-coordinate structures in solution, although they dissociate to some extent to HgX_2 and X^- [205]. Mercury in the binary HgX_2 compounds (X = Cl, Br, I) apparently has linear, octahedral, and tetrahedral coordinations, respectively, in the solid state [206]. Halide ions add to $Hg(CF_3)_2$ to give $Hg(CF_3)_2X^-$ complexes, which may be three-coordinate [207]. The compound $HgBr_2(PhPEt_2)$ is dimeric and four-coordinate in benzene, but the dimer is partially dissociated in acetone, presumably to form the three-coordinate monomer.

The empirical formula of $(HgCl_2)_2L$ (L is 1,6 dithiacyclododeca-*cis*-3,8-diene) suggested three-coordinate mercury atoms, but an X-ray study revealed a rather novel polymeric structure (Q) which contains one distorted tetrahedral mercury atom that is bridged loosely by two chlorine atoms to a slightly distorted mercuric chloride molecule [200]. On the other hand,



(O)

$HgCl_2$ (tetrahydrothiophene) is reportedly ionic and contains two-coordinate $[HgLCl]^+$ cations [182,183].

The structure of chlorobis(2-thiouracil)copper(I) · DMF contains a nearly planar $CuClS_2$ coordination unit with the dimethylformamide molecule simply filling a hole in the lattice (Fig. 24) [208]. The geometry around copper is almost trigonal-planar with the copper atom being located ~0.1 Å out of the plane of the sulfur and chlorine atoms. The Cu—Cl and Cu—S distances (Fig. 24) are both at least 0.1 Å shorter than those found in analogous tetrahedral Cu(I) complexes, which is a contraction comparable to those found in the Cu—S and Cu—Cl distances discussed above for the trigonal-planar Cu(I) complexes of trimethylphosphine sulfide and substituted thioureas.

Pseudohalides. The copper(I) cyanide system is very complicated, with a variety of possible formulations. The equilibria of Group IB—cyanide complexes have been studied in aqueous solution [209—210]. Equilibrium con-

$$CN^- + Cu(CN)_2^- \underset{K_{3,2}}{\rightleftharpoons} Cu(CN)_3^{2-} \overset{CN^-}{\underset{K_{4,3}}{\rightleftharpoons}} Cu(CN)_4^{3-} \qquad (36)$$

stants for these reactions are $K_{4,3}$ ($7.6 \cdot 10^3$ mol l^{-1}) and $K_{3,2}$ ($2.44 \cdot 10^5$ mol l^{-1}). Thus, the trigonal-pyramidal ion $[Cu(CN)_3]^{2-}$ has considerable stability in aqueous solution [211]. In fact, the anion has been isolated

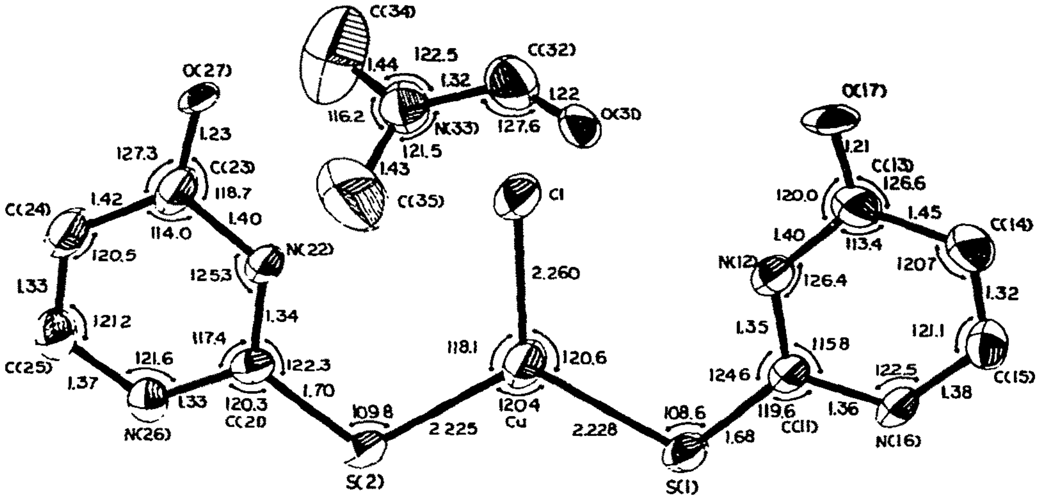


Fig. 24. An ORTEP drawing of the chloro-bis(2-thiouracil)copper(I) molecule and of a dimethylformamide molecule of solvation. Reproduced with permission from ref. 208.

in the compound [Cu(ethylenediamine)$_3$] [Cu(CN)$_3$] and a crystal structure determination was reported to be underway [212]. Similar equilibria have been studied in the silver cyanide system [210]. For silver the values of $K_{4,3}$ and $K_{3,2}$ are 3.18 and 0.113, respectively; thus, the three-coordinate ion $[Ag(CN)_3]^{2-}$ does not have considerable stability in aqueous solution. Raman studies on the ion $[Hg(CN)_3]^-$ indicate that it undergoes extensive disproportionation in aqueous solution (eqn. 37) [213,214].

$$2[Hg(CN)_3]^- \rightarrow Hg(CN)_2 + [Hg(CN)_4]^{2-} \qquad (37)$$

Cromer and co-workers have studied crystallographically a number of polynuclear copper cyanide compounds and several contain three-coordinate copper. The structure of $KCu(CN)_2$ has a spiral (Fig. 25) of $[Cu(CN)_2]^-$ chains about a two-fold screw axis, with equal numbers of bridging and terminal cyanide groups [215]. An approximately trigonal-planar environment around each copper atom is composed of one terminally bonded cyanide (Cu—C = 1.92 Å) and two bridging cyanides (Cu—C = 1.92 Å, Cu—N = 2.05 Å). Bond angles around copper range from 107.3 to 134.2°. This structure is markedly different from the structures of $KAg(CN)_2$ and $KAu(CN)_2$, both of which have ionic structures with discrete, linear, two-coordinate $[M(CN)_2]^-$ ions [216,217].

The structure of $KCu_2(CN)_3 \cdot H_2O$ is similar to that of $KCu(CN)_2$ and contains a spiral chain of $[Cu_2(CN)_3]^-$ units, with the potassium ions and uncoordinated water molecules filling channels in the structure between the chains [218]. Every cyanide group functions as a bridging ligand and each

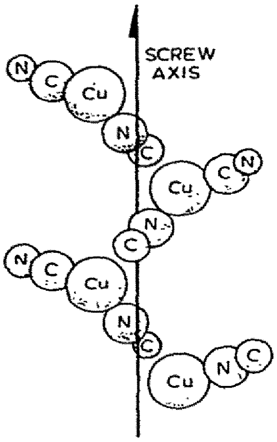


Fig. 25. A drawing of the $[Cu(CN)_2^-]_\infty$ polymer chain. The view is normal to *y* at an angle such that all of the copper atoms are in the plane of the paper. Adapted with permission from ref. 215.

copper atom is approximately trigonal planar. One of the two copper atoms in the asymmetric unit is bonded to two carbon atoms (Cu—C = 1.89, 1.90 Å) and one nitrogen atom (Cu—N = 1.98 Å); the copper atom lies 0.07 Å out of the C_2N coordination plane and bond angles around copper are 111, 114, and 134°. The other copper atom is bonded to two nitrogen atoms (Cu—N = 1.96, 2.02 Å) and to one carbon atom (Cu—C = 1.87 Å); it lies 0.19 Å out of the N_2C coordination plane and its bond angles are 109, 115, and 133°.

The structure of the mixed valence compound, $Cu_3(NMe_3)_3(CN)_4$, consists of infinite, nearly-planar, polymeric sheets that contain pentacoordinate Cu(II) ions and three-coordinate Cu(I) ions in a 1 : 2 ratio (Fig. 26) [219]. All the cyanide ions function as bridging ligands and link the copper-contain-

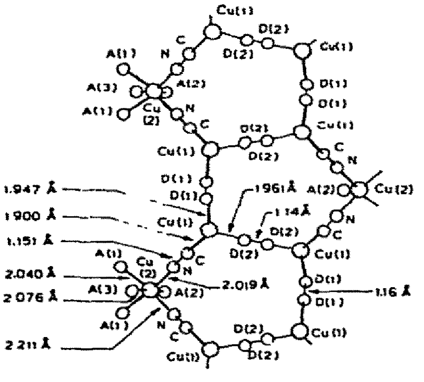


Fig. 26. A segment of the polymeric chains in $Cu_3(NMe_3)_3(CN)_4$ viewed along the *b* axis. Adapted with permission from ref. 219.

ing polyhedra to form infinite sheets. The Cu(I) atoms have a distorted trigonal-planar coordination, with bonds to the carbon atom of the ordered cyanide group and the ends of two disordered cyanide groups. The three angles at Cu(I) are in the range 111.3—124.5°.

Cooper and Plane [220] have prepared the three-coordinate cyanide complexes Cu(N—N)CN by using the bidentate N—N nitrogen ligands *o*-phenanthroline and bipyridyl. These complexes are monomers in 2-aminoethanol and in the solid state, as judged by molecular weight and infrared measurements. Ahuja and Rao [221] reported the synthesis and characterization of $HgL(CN)_2$ complexes where L = quinoline or a substituted quinoline. The compounds are non-electrolytes in dimethylformamide and monomers in ethanol. Infrared spectra of the solids show only one C—N stretching frequency near 2180 cm^{-1}; thus, the complexes appear to be three coordinate.

The structure of $AgClO_2$ contains infinite sheets with planar, three-coordinate silver atoms [222]. The three atoms (one chlorine and two oxygens) surrounding silver come from three different chlorite ions and the bond distances are Ag—Cl, 2.20 Å and Ag—O, 2.22 Å. The closest axial contact is 3.36 Å (Ag—O).

Recently, Coucouvanis et al. [223] isolated orange-red crystals of the composition $(Ph_4P)_2Cu(SPh)_3$ by treating the Ph_4P^+ salt of bis(dithiosquarato)copper(II) dianion, $(Ph_4P)_2Cu(DTS)_2$, with four equivalents of KSPh in boiling acetonitrile. Magnetic measurements and a structure determination confirmed that the compound contains the discrete copper(I) anion $[Cu(SPh)_3]^{2-}$. The copper atom lies only 0.05 Å from the S_3 plane, but other deviations from exact trigonal symmetry are shown by the Cu—S bond lengths and S—Cu—S bond angles (Fig. 27). The longest Cu—S bond (2.335(3) Å) is opposite the largest S—Cu—S angle (135.4(2)°). This anion, $[Cu(SPh)_3]^{2-}$, reacts readily with a Cu(I) salt to give $[Cu_2(SPh)_3]^-$, which undergoes oligomerization to produce the cluster $[Cu_4(SPh)_6]^{2-}$, which also contains trigonal copper(I). (See Section IIIg (i) for a discussion of the structure of $[Cu_4(SPh)_6]^{2-}$.)

(e) Binary carbonyl, dinitrogen and dioxygen complexes

A recently developed technique is proving useful for obtaining simple binary transition metal complexes of low coordination number which are difficult, if not impossible, to prepare by conventional procedures. The method involves the matrix co-condensation reactions of metal atoms with neutral ligand molecules such as CO, CS, CS_2, COS, N_2, and O_2 at cryogenic temperatures, i.e. 4.2—20 K [224,225]. Some binary, three-coordinate metal complexes that have been synthesized recently and characterized by matrix isolation methods are listed in Table 12. Also, a number of "mixed" dioxygen—dinitrogen and dinitrogen—carbonyl complexes have been synthesized by Ozin and co-workers [252,253]. In this review, we shall focus on the three-coordinate binary complexes.

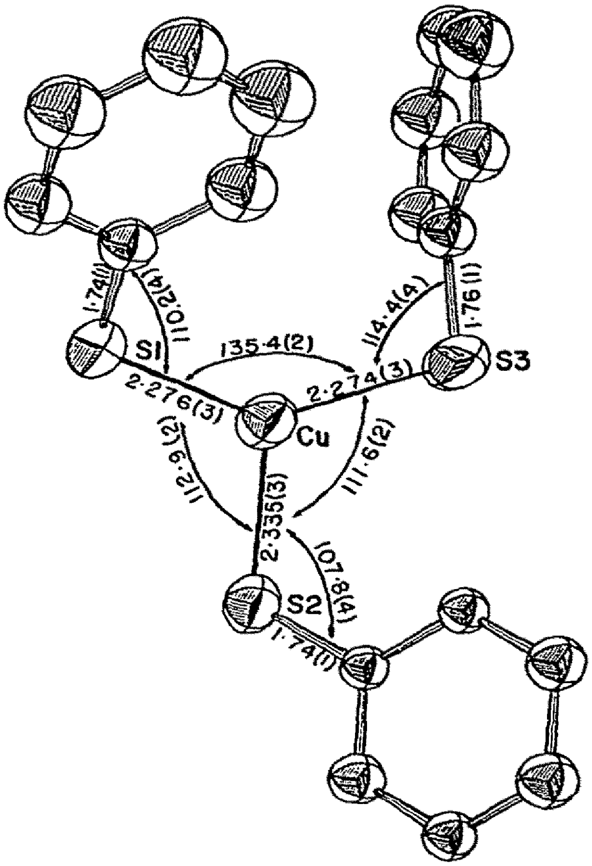


Fig. 27. The structure of the anion $[Cu(SPh)_3]^{2-}$. Reproduced by permission of D. Coucouvanis, ref. 223.

The identities of the binary compounds have been ascertained almost totally by matrix infrared and Raman spectroscopy. Since this method is subject to several technical difficulties, including the reproducible preparation of matrices, matrix-induced geometric perturbations, mixtures of products, and ambiguity in band assignment, the geometrical assignments discussed below should be considered tentative in many cases.

Matrix infrared and Raman spectroscopy for the d^{10} carbonyl [226,227, 229] and dinitrogen [240—243] complexes of the types $M(CO)_3$ and $M(N_2)_3$ (M = Pt, Pd, Ni) have been interpreted in terms of trigonal-planar structures. Isotopic frequencies have been computed for the N≡N and C≡O stretching modes of the $M(N_2)_3$ and $M(CO)_3$ complexes, respectively, on the basis of the Cotton—Kraihanzel force field approximation for D_{3h} symmetry and they are in close agreement with the observed values. Spectral data on these three coordinate dinitrogen and carbonyl complexes are given in Tables 13

TABLE 12

Mononuclear, three-coordinate carbonyl compounds characterized from metal atom—carbon monoxide matrix reactions

Carbonyl	Probable geometry	Metal *d*-electron configuration	Ref.
$Ni(CO)_3$	D_{3h}	10	226
$Pd(CO)_3$	D_{3h}	10	227, 228
$Pt(CO)_3$	D_{3h}	10	229
$Co(CO)_3$	C_{3v}	9	230,231,246
$Rh(CO)_3$	*	9	230
$Ir(CO)_3$	*	9	230
$Cr(CO)_3$	C_{3v}	6	231
$Ta(CO)_3$	D_{3h}	5	226
$U(CO)_3$	*		232
$La(CO)_3$	*		233
$Mn(CO)_3$	*	7	234
$Fe(CO)_3$	C_{3v}	8	235
$V(CO)_3$	C_{3v} or D_{3h}	5	236
$Re(CO)_3$	*	7	231
$Cu(CO)_3$	D_{3h}[a]	10	237,238
$Ag(CO)_3$	D_{3h}[a]	10	239

* Blank entries denote unknown geometry.

[a] In argon matrix; C_2 in pure CO.

TABLE 13

Vibrational spectral data on three-coordinate, binary transition metal dinitrogen and carbonyl complexes [a, b]

ML_3 complex	ν_{NN}	ν_{MN}	ΔH_c [c]	k_{NN} [d]	k_{MN} [d]	Ref.
$Ni(N_2)_3$	2134.0	343	9.66	19.38	1.26	243
$Pd(N_2)_3$	2242.0	350	4.89	20.97	1.61	243
$Pt(N_2)_3$	2211.5	390	6.51	20.43	2.40	243
$Rh(N_2)_3$	2196	—	6.78	20.17	—	242
	ν_{CO}	ν_{MC} [e]		k_{CO} [e]	k_{MC}	
$Ni(CO)_3$	2017			17.00		
$Pd(CO)_3$	2060			17.35		
$Pt(CO)_3$	2049			17.24		
$Cu(CO)_3$	2010	375—325		16.47	1.35	238
$Ag(CO)_3$	1958	250		16.11	0.82	239

[a] All frequencies are in cm^{-1}.

[b] The structures in an argon matrix are trigonal planar.

[c] ΔH_c is the enthalpy of decomposition of the compound to the metal atom and free ligand; $\Delta H_c \propto n \Delta H_{ML}$, where n is the coordination number with respect to the ligand. The average metal—ligand bond energy is given by $\Delta H_{ML} \propto k^{L}_{C.K.} - k$ where k^{L} and $k^{L}_{C.K.}$ are the free ligand and Cotton—Kraihanzel bond stretching force constants respectively.

[d] Cotton-Kraihanzel force constants in mdyn/Å calculated from observed infrared and Raman frequencies.

[e] Unfortunately, to date it has not been possible to observe the M—C stretching modes for some of the tris-carbonyl complexes $M(CO)_3$.

TABLE 14

Comparison of frequency and decreases of the bond stretching force constant for tris-dinitrogen and -carbonyl complexes of nickel(0), palladium(0), and platinum(0)

ML_3 complex	$\Delta\nu$ *, cm^{-1}	ΔF ** mdyn/Å	Ref.
$Ni(N_2)_3$	191	3.22	240
$Pd(N_2)_3$	87	1.63	240
$Pt(N_2)_3$	116	2.17	241
$Ni(CO)_3$	121	1.46	240
$Pd(CO)_3$	78	1.11	240
$Pt(CO)_3$	90	1.22	241

* $\Delta\nu$ = the increase of the stretching frequency on formation of the complex.
** $\Delta F = k^{L} - k^{L}_{C-K}$ where k^{L} and k^{L}_{C-K} are the free ligand and Cotton-Kraihanzel stretching force constants, respectively.

and 14, respectively. The anion $Ni(CO)_3^-$ has been made recently in an argon matrix at 10 K, and it also appears to be a planar species [244]. Infrared intensity data [245] for the d^6 species $Mo(CO)_3$ and $Cr(CO)_3$ indicate a pyramidal C_{3v} geometry.

Recent work in Ozin's laboratory provides evidence for formation of dinitrogen complexes of other metals, e.g. Cr, Cu, Fe, Ir, and W [225]. Although silver forms the carbonyl complexes $Ag(CO)_n$ (n = 1—3), co-condensation of dinitrogen with silver gave no evidence for the corresponding $Ag(N_2)_n$ complexes [225]. The characterized dinitrogen complexes are of the type $M(N_2)_n$, where n = 1—4 for M = Ni, Co, and Rh [225,226,240,243,246] and n = 1—3 for Pd [240,243] and Pt [240,243,247]. With the exceptions of $Co(N_2)_2$, [248] and $Pt(N_2)_2$ [241], which may have "sideways" bonded dinitrogen, all the binary dinitrogen complexes have N_2 bonded in an "end-on" fashion with a linear or near linear M—N—N linkage. In contrast, all the mono- and bis-dioxygen complexes contain O_2 units bonded to the metal atom in a "sideways" manner [249] with a D_{2d} "spiro"-type structure favored for the bis-complexes.

The vibrational spectroscopy data indicate that the bonding properties of the dinitrogen and carbonyl molecules in the binary ML_n complexes are very similar to dinitrogen and carbonyl complexes that are stable at room temperature, and the following generalizations can be made.

(1) Coordinated N_2 gives rise to new stretching frequencies that are shifted 100—200 cm^{-1} to lower values compared to gaseous N_2 (Table 13). In fact, the $\Delta\nu_{N_2}$ is greater than $\Delta\nu_{CO}$ for an analogous complex (Table 14).

(2) A monotonic increase in the N≡N and C≡O stretching force constant is observed with increasing coordination number around the metal.

(3) The ΔHc function ($n\Delta F$) increases monotonically with n in the order Ni > Pt > Pd.

(4) The Cotton—Kraihanzel force-field approximation is successful in

predicting both N≡N and C≡O stretching frequencies in binary dinitrogen and carbonyl complexes, respectively.

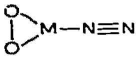
(5) Metal geometries in corresponding $M(N_2)_n$and $M(CO)_n$ complexes are similar.

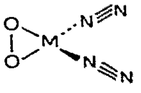
As indicated in Table 14 by the quantity ΔF_{N_2} or ΔF_{CO}, the strength of the M—L interaction in the three-coordinate, binary dinitrogen and carbonyl complexes is Ni > Pt > Pd. The increased stability of the platinum complexes, relative to those of palladium is probably a manifestation of the lanthanide contraction, and is consistent with the promotion energy requirements [250] and the Allred—Rochow electronegativities $[\chi_{Ni}(1.75) > \chi_{Pt}(1.44) > \chi_{Pd}(1.35)]$ of the respective metals.

Ozin and co-workers have characterized the thermally unstable copper carbonyl complexes by the matrix co-condensation techniques [238]. The $Cu(CO)_3$ complex has a deep purple color and its electronic spectrum, which was recorded in a pure CO matrix, is dominated by two intense absorptions at 562 and 375 nm, with two much weaker shoulders at 495 and 344 nm. The two intense bands probably are the $^2A_2'' \rightarrow {}^2A_1'$ and $^2A_2'' \rightarrow {}^2E''$ transitions, respectively, the former being between orbitals that are mainly copper in character and the latter being a copper to CO charge-transfer transition. The weak shoulders at approximately 495 and 344 nm most probably arise from a matrix site effect [238]. Two $Cu(CO)_3$ units form the dimeric molecule $Cu_2(CO)_6$, which can be viewed as having a Cu—Cu single bond created by overlap of the singly occupied, highest orbital of each $Cu(CO)_3$ fragment, analogous to the scheme proposed for $Mn_2(CO)_{10}$ [251].

The electronic absorption spectrum of $Cu_2(CO)_6$ is dominated by an intense transition at 417 nm, which by analogy with the work of Gray and co-workers [251] can be associated with the strongly allowed $^1A_1 \rightarrow {}^1A_2$ ($\sigma \rightarrow \sigma^*$) electronic transition involving orbitals arising from the copper—copper interaction. From a comparison of the enthalpies for reactions of several metal—metal bonded carbonyls (that are stable at room temperature) and the values of their corresponding σ—σ^* transition, it has been concluded that the extremely low σ—σ^* transition energy of $Cu_2(CO)_6$ reflects a correspondingly low Cu—Cu bond dissociation energy (or Cu—Cu bond stretching force constant) and is consistent with the inability, so far, to synthesize $Cu_2(CO)_6$ by conventional chemical techniques.

The products of the co-condensation reactions of Ni, Pd, and Pt atoms with mixtures of O_2, N_2, and Ar at 6—10 K gave matrix isolation infrared spectra for "mixed" dioxygen, dinitrogen complexes of the type $M(O_2)(N_2)_m$ (m = 1 or 2) [252,253]. The structures are given below, and either formula





type could be considered as three-coördinate, depending on whether the "side-on" dioxygen unit is regarded as a monodentate or as a bidentate ligand. In general, the "mixed" dioxygen, dinitrogen complexes tend to have higher N—N stretching frequencies, but essentially the same O—O stretching frequencies as the parent $M(N_2)_n$ and $M(O_2)_n$ compounds [255].

No tris-dioxygen complexes of nickel, palladium, or platinum, analogous to the binary dinitrogen $M(N_2)_3$ or mixed $M(O_2)(N_2)_2$ complexes, are presently known. The absence of $M(O_2)_3$ complexes probably is associated with the preference of dioxygen for "side-on" bonding. Such an $M(O_2)_3$ complex would require a pseudo-six-coordinate metal. Thus, binary tris-dioxygen complexes are more likely with the early members of the transition series, e.g. a d^6 M(O) configuration such as chromium, molybdenum, or tungsten.

Co-condensation of nickel with CS, which has been produced from an electrical discharge of CS_2/Ar mixtures, gave the thiocarbonyls $Ni(CS)_n$ (n = 1—4) [254,255]. An unusual feature of the infrared spectra of $Ni(CS)_4$, $Ni(CS)_3$, and $Ni(CS)_2$ is that the C—S stretching frequencies all lie *above* that of free CS, whereas all known carbonyls (except $NiX_2 \cdot CO$) have their C—O stretching frequencies *below* that of free carbon monoxide. This change in behavior was interpreted in terms of a relative difference in σ-donor and π-acceptor properties of the CS ligand as compared to CO.

DeKock and Van Leirsburg [256] found that NiF_2 and $NiCl_2$co-condense with carbon monoxide and dinitrogen to give three-coordinate $NiX_2 \cdot CO$ and $NiX_2 \cdot N_2$ complexes, respectively, in which the carbonyl and dinitrogen ligands function primarily as σ-donors. The bonding properties of CO and N_2 in these complexes closely resemble those of the $M(O_2)(N_2)$ complexes discussed above.

Several authors have used theoretical calculations to predict structures of the ML_3 fragments [257—259]. While the results of the calculations differ slightly in detail, in general they agree among themselves and with the observed structures given in Table 15. However, in a few cases the calculated

TABLE 15

Predicted and observed geometries for $M(CO)_3$ species

Species	Calc. geom.	Obs. geom.	Ref.
$V(CO)_3$	C_{3v},$^{a-d}$ D_{3h},^{b,c,e}	C_{3h} or D_{3h}	
$Cr(CO)_3$	C_{3v},^{a,b,d} D_{3h},^{b,e} C_{2v},^{c,e}	C_{3h}	
$Mn(CO)_3$	C_{3v},^{a} C_{2v},$^{b-d}$ D_{3h},^{b,e}	f	
$Fe(CO)_3$	C_{2v},$^{a-d}$ C_{3v},^{b,e}	C_{3v}	260
$Co(CO)_3$	C_{3v},^{a} C_{2v},^{b,c}	C_{3v}	246
$Ni(CO)_3$	C_{3v},^{a} D_{3h} ^{b}	D_{3h}	261
$Cu(CO)_3$ $Ni(CO)_3^-$		D_{3h}	238,244

[a] Hoffmann orbital-based calculation. [b] Burdett's MIE calculation. [c] Jahn—Teller considerations. [d] Low spin. [e] High spin. [f] Geometry not yet established.

[257—259] and observed geometries show minor discrepancies. Whereas Hoffmann's calculation [259] slightly favors (by only ca. 1 kcal mol^{-1}) a C_{3v} geometry, all known three-coordinate d^{10} $M(CO)_3$ (M = Ni, Pd, Pt) and $d^{10}s^1$ species $Cu(CO)_3$, $Ag(CO)_3$, and $Ni(CO)_3^-$ appear to be trigonal-planar [226, 227,229]. However, one must remember that the observed geometries are usually assigned from the absence or observation of the totally symmetric CO stretching vibration in the infrared spectrum. As this vibration will be very weak for a nearly planar $M(CO)_3$ structure, definitive assignment is difficult unless supported with isotopic data and Raman studies. This point is illustrated by the matrix isolation vibrational study on $Co(CO)_3$, which indicated D_{3h} symmetry for the molecule [246]. A C_{3v} pyramidal geometry for $Co(CO)_3$ was established only with the aid of an ESR spectrum [246].

(f) Olefin ligands

Recent studies have revealed several trigonal-planar complexes with d^{10} metals containing only olefin and alkyl ligands [262,263]. Of special significance has been the discovery that three-coordinate olefin complexes are key intermediates in some important catalytic schemes, including the Ziegler process [264, 265].

Nickel, palladium, and platinum. Wilke et al. [265] have prepared Ni(ethylene)$_3$, the parent of all nickel—olefin compounds, by direct displacement of 1,5,9-cyclododecatriene (eqn. 38). A trigonal-planar arrangement around nickel is postulated for this compound, as well as for the nickel(0) complex of *all-cis*-1,5,9-cyclododecatriene and tris(bicycloheptene)nickel [266]. Tris(ethylene)nickel(0) reacts quantitatively with $Al(n\text{-}Bu)_3$ (catalytically with an excess of ethylene and $Al(n\text{-}Bu)_3$) to give butene, triethylaluminum, and elemental nickel. This reaction is claimed to be a key step in the "nickel effect" that was discovered by Ziegler and Holzkamp [265]. Tris(ethylene) nickel(0) is a pale yellow, crystalline, air- and moisture-sensitive solid. A structure determination has not been reported for this interesting compound, but a closely related compound, tris(bicyclo[2.2.1]heptene)nickel(0), has been studied crystallographically [266]. Results on the latter compound show that the olefin ligands are in an all *cis* configuration, which gives a regular trigonal-planar arrangement of olefinic bonds around the nickel atom.

$$3C_2H_4 + Ni(1,5,9\text{-}CDT) \xrightarrow[0°C]{Et_2O} Ni(C_2H_4)_3 + 1,5,9\text{-}CDT \qquad (38)$$

The tris(ethylene)platinum(0) complex, $Pt(C_2H_4)_3$, was prepared recently by Stone's group [267] by displacing cyclo-octadiene from $Pt(C_8H_{12})_2$ with ethylene at room temperature. The proposed structure for $Pt(C_2H_4)_3$ has the platinum atom and C=C bonds coplanar, which is analogous to the structure of tris(bicyclo[2.2.1]heptene)nickel(0) that was discussed above. This tri-

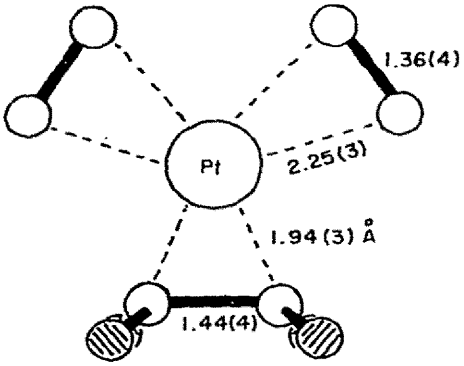
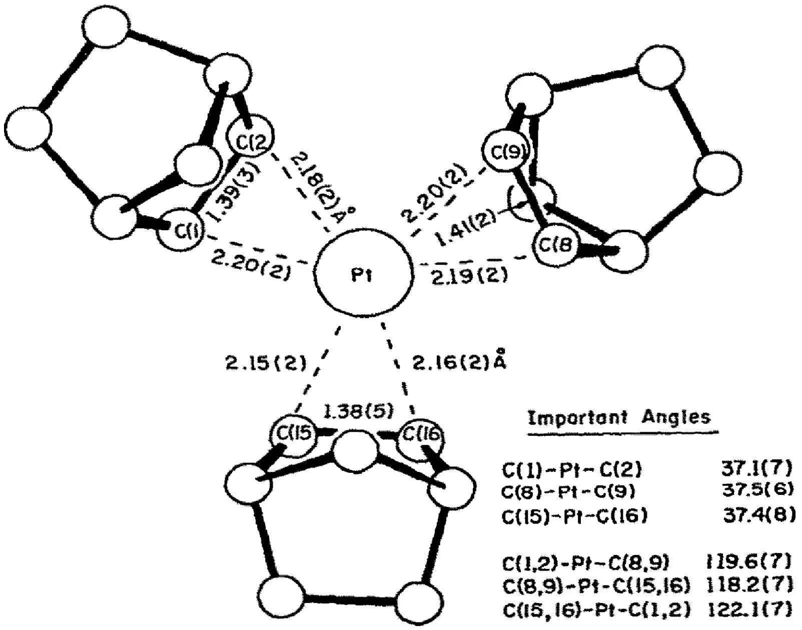


Fig. 28. A perspective drawing of the molecular structure of $[Pt(C_2F_4)(C_2H_4)_2]$. Adapted with permission from ref. 268.

gonal-planar structure and the coplanar arrangement of double bonds has also been found very recently in the structures of the three complexes $[Pt(C_2F_4)(C_2H_4)_2]$, $[Pt(C_7H_{10})_3]$, and $Pt(PMe_3)(C_2H_4)_2$ [268]. The three olefinic double bonds of $Pt(C_2F_4)(C_2H_4)_2$ (Fig. 28) lie in the coordination plane of the platinum atom with Pt—C distances for Pt—C(F_2) and Pt—C(H_2) of 1.97(3) Å and 2.25(3) Å, respectively.



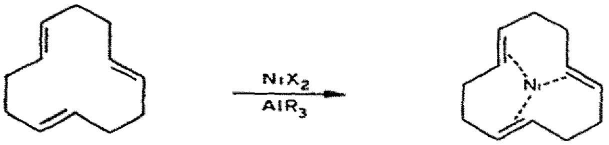
Important Angles

C(1)-Pt-C(2)	37.1(7)
C(8)-Pt-C(9)	37.5(6)
C(15)-Pt-C(16)	37.4(8)
C(1,2)-Pt-C(8,9)	119.6(7)
C(8,9)-Pt-C(15,16)	118.2(7)
C(15,16)-Pt-C(1,2)	122.1(7)

Fig. 29. A perspective drawing of the molecular structure of [Pt(bicyclo[2.2.1]-heptene$)_3$]. Adapted with permission from ref. 268.

The molecular structure of tris(bicyclo[2.2.1]heptene)platinum(0) is trigonal planar and contains the double bonds of the three bicyclo[2.2.1]-heptene ligands in the coordination plane of the platinum atom, at a mean Pt—C distance of 2.23(3) Å (Fig. 29) [268]. At the reported stage of refinement, the maximum deviation from this plane is 0.06 Å. The mean C═C bond length is 1.38 Å, which is essentially the same as found for coordinated ethylene in $Pt(C_2F_4)(C_2H_4)_2$. Tris(bicyclo[2.2.1]heptene)palladium(0), $Pd(C_7H_{10})_3$, is isostructural with the platinum(0) complex [268]. Addition of one equivalent of tricyclohexylphosphine or trimethylphosphine to $Pt(C_2H_4)_3$ gives crystalline complexes of the type $Pt(C_2H_4)_2(PR_3)$. NMR data show that the latter complexes are fluxional at room temperature, but "frozen out" with a trigonal-planar arrangement of ligands at low temperature [268].

The largest number of isolated three-coordinate binary olefin complexes are of nickel(0), primarily resulting from Wilke's research group [265]. One of the interesting catalytic syntheses involves the preparation of 1,5,9-cyclododecatriene (CDT) from butadiene in the presence of nickel. The three-coordinate, *trans, trans, trans*-1,5,9-cyclododecatriene complex of nickel(0), (CTD)Ni(0), was prepared by reducing nickel(II) with aluminum alkyls in the presence of the triene (eqn. 39). Deep-red needles of (CDT)Ni(0) can be sublimed in vacuo; infrared spectra indicate that the nickel atom is bound to all three double bonds of the cyclododecatriene. The compound is monomeric in both the vapor phase and in solution. Brauer and Krüger [269] have determined the crystal structure of the complex *trans, trans, trans*-1,5,9-cyclododecatrienenickel(0) (Fig. 30). If one assigns the center of each olefinic bond as a coordination position, the nickel atom has a trigonal-planar coordination with crystallographic C_2 and accidental D_3 symmetry. The Ni—C lengths are 2.026 Å, and each olefin is twisted by 32° from the plane formed by nickel and the centers of the C—C bonds.



(39)

The nickel atom in (CDT)Ni(0) is coordinatively unsaturated (a 16-electron case); consequently the complex readily adds another ligand; also the cyclododecatriene can be displaced easily by other ligands. Such reactions are illustrated in Scheme V.

The complex (CDT)Ni(0) is a catalyst for cyclo-oligomerization of butadiene to cyclododecatriene [265]. When excess butadiene is treated with (CDT)Ni(0), the cyclododecatriene already present in the complex is displaced and new cyclododecatriene is produced in the homogeneous phase in a smooth reaction. At −40° C the CDT is also displaced by butadiene but no

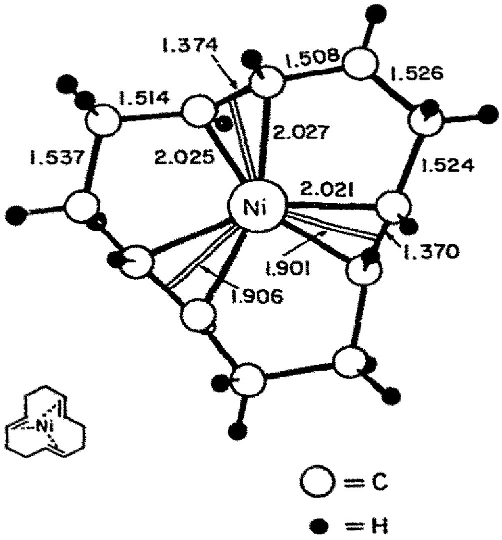
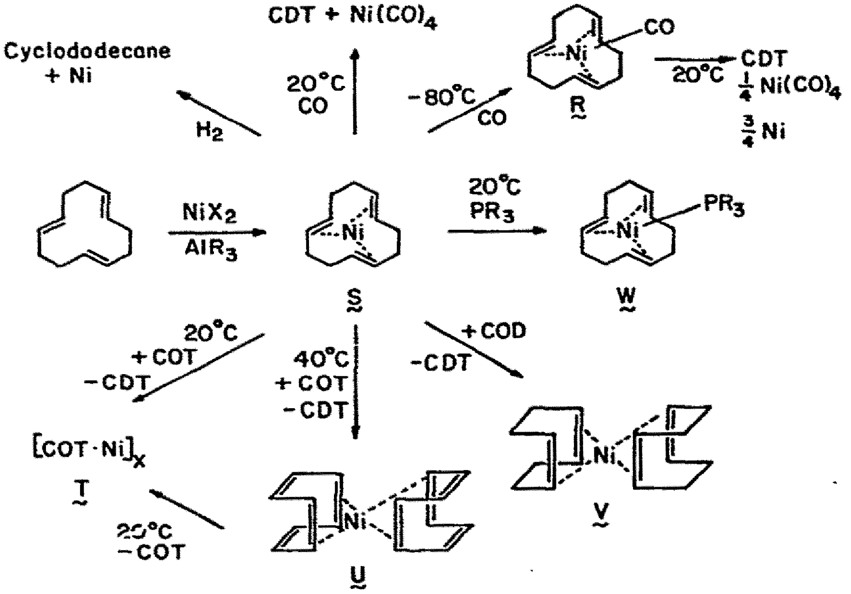


Fig. 30. A perspective drawing of all-*trans*-1,5,9 cyclododecatrienenickel(0). Adapted with permission from ref. 269.

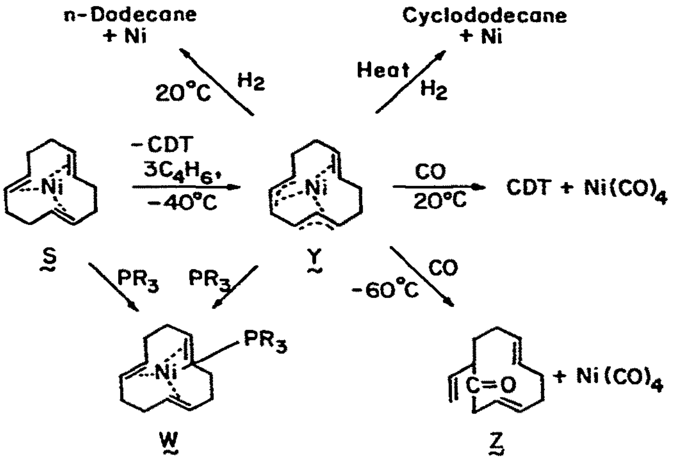
new CDT is formed. Each mole of catalyst takes up exactly three moles of butadiene and a compound of formula $C_{12}H_{18}Ni$ crystallizes below 20°C; structure (Y) is assigned to this compound. Some of the reactions of (Y) are illustrated in Scheme VI. Hydrogenation to *n*-dodecane is practically quanti-

Scheme V

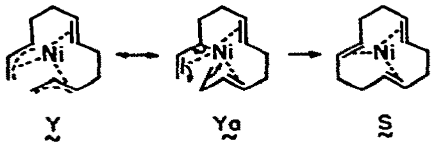


tative at 20° C and electron donors (e.g. butadiene, carbon monoxide, or phosphines) cause liberation of cyclododecatriene.

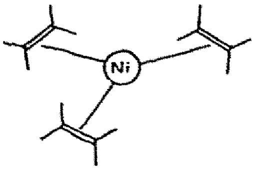
Scheme VI



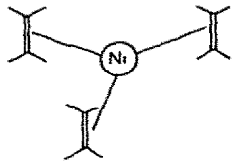
On the basis of the above reactions, the sequence postulated for the cyclo-oligomerization reaction is displacement of the original cyclododecatriene and then linking of three butadiene molecules on nickel, resulting in formation of a C_{12}-chain containing a *trans* double bond and two terminal π-allyl groups. Ring closure can then be effected by the influence of heat or electron donors to give either the three-coordinate (CDT)Ni(0) or the four-coordinate Ni(CDT)B, where B is a Lewis base. A possible electron shift sequence is given below.



Reaction of nickel acetylacetonate with triethylaluminum in ether with *cis, cis, trans*-CDT or *trans, trans, cis*-CDT gives pale red crystals of Ni(CDT), which is very soluble and easily decomposed [266]. These two CDT complexes react readily with *all cis*-CDT to yield the more stable compound Ni(*all-cis*-CDT). The latter compound reacts readily with carbon monoxide to give $Ni(CO)_4$ and *all-cis*-CDT. The proton NMR spectrum shows only two peaks in a 1 : 2 ratio, corresponding to the methylene and olefinic protons and consistent with a symmetrically bonded ligand in the crown conformation. The relatively greater stability for the *all-cis* CDT complex compared to the *trans, cis, cis* and the *trans, trans, cis* complexes may be due to all three olefinic linkages being coplanar with the nickel atom in complexes of *all cis*-CDT, but not with the other two ligands. This postulate is supported by the structures of all known tris-olefin complexes, which prefer the "all-planar" geometry represented by (A) below.

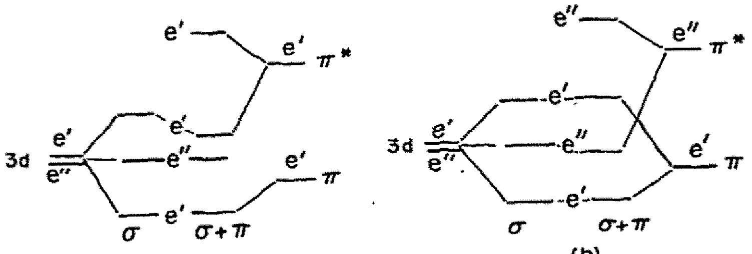


A, D_{3h}



B, D_{3h}

Molecular orbital calculations indicate that conformation (A) is favored by 0.74 eV over conformation (B) [90]. On the basis of symmetry, the metal—olefin σ-interactions should be virtually identical in both cases; thus the preference for the all-planar configuration must be due to more favorable $d\pi \rightarrow \pi^*$ back-bonding. A rationalization of this preference may be obtained from Fig. 31, which shows only those metal and ligand orbitals involved in the σ and π bonding. In both cases, the σ-bonding raises the nickel e′ level. In the all-planar case, the e′ orbital is depressed by a strong interaction with the ethylene π^* orbital of identical symmetry. In the all-upright case, the π interaction is with the e″ orbital. Since the e″—π^* energy separation is larger that the e′—π^* gap, the interaction is weaker in the former case; hence, less stabilization results from the all-upright case. The charge density distribution, deduced from a Mulliken population analysis, indicates a net charge on nickel of +0.624 and +0.839 in the all-planar and all-upright conformations, respectively. This result also indicates greater π-backbonding in the all-planar case. The difference appears to be due largely to the lower occupation of the metal π-back donating orbitals in the all-planar case (d_{xy}, $d_{x^2-y^2}$, 1.73 charge units) compared to the all-upright case (d_{xz}, d_{yz}, 1.81 charge units). Consis-



(a) (b)

Fig. 31. Schematic decomposition of π bonding in $(C_2H_4)_3Ni$. At left is the all-planar structure (a); at right, the upright structure (b). The orbital interactions are analyzed in stages. First, interaction with the ethylene π levels is turned on, in the columns marked σ. Second, the mixing with the ethylene π^* levels is added, in the columns marked $\sigma + \pi$. Adapted with permission from ref. 259.

tent with better back-donation in the all-planar structure, the overlap population of the C—C bond is smaller in this case (1.266 vs. 1.312 in the all-upright case and 1.304 in free ethylene).

An alternative explanation for the greater stability of the all-planar case derives from the prediction that π-acceptor orbitals are favored in the equatorial plane of trigonal-planar and trigonal-pyramidal complexes. This effect is due to in-plane hybridization of metal *d*- and *p*-orbitals, leading to more directional and effective bonding with in-plane acceptor orbitals.

Copper and silver. The affinity of univalent Group IB metal ions for olefins has long been recognized. Recent structural studies have shown that many of these complexes contain three-coordinate metals [270,271]. For example, the 1 : 1 complex of cyclooctatetraene (COT) and cuprous chloride has an infinite chain structure with single-chloride bridges between copper atoms [272]. Each copper has approximately trigonal-planar coordination arising from two chlorides and one olefinic linkage of the COT ligand. Angles at copper range from 106.0 to 130.1°, the Cu—Cl distances are 2.288 and 2.284 Å, and the Cu—C distances are 2.073 and 2.097 Å. No other Cu—C distances in this structure are shorter than 2.755 Å (Fig. 32). Note that the sum of the angles around copper from the two COT molecules and the shortest Cu—Cl bond total 359°, providing evidence for the trigonal nature of the copper atom. Although this structure is formally related to that of $Cu_2Cl_2(PPh_3)_3$ and $Cu_2I_2(PPh_3)_3$ (Fig. 14), both copper atoms are trigonally bonded in the olefin complex [272].

Apprpximately trigonal-planar coordination has also been observed in the

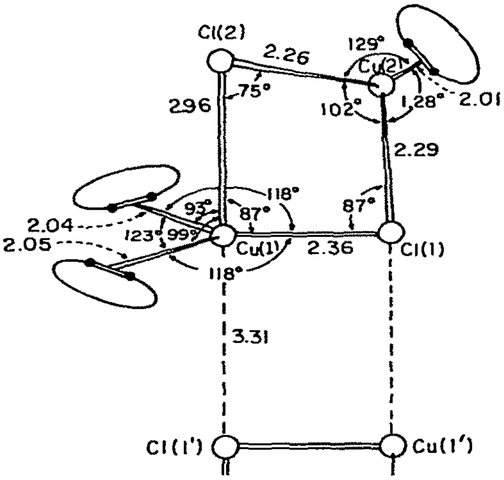


Fig. 32. A drawing of the coordination geometry about the copper atoms in $[Cu_2Cl_2(C_8H_{14})_3]$. If the long Cu(1)—Cu(2) separation (2.96 Å) is considered as non-bonding, the effective geometry around each copper is trigonal planar. Adapted with permission from ref. 272.

1 : 1 COT complex of $AgNO_3$ [273]. The complex is very similar to the CuCl(COT) complex discussed above, in that continuous silver nitrate chains are found in the structure. The silver atom forms strong bonds to two oxygen atoms (2.36, 2.43 Å) and to one olefin linkage (Ag—C = 2.46, 2.51 Å) lying in the AgO_2 plane. Also, a weak axial interaction (Ag—C = 2.8 Å) is present in the $AgNO_3$(COT) complex analogous to that in the CuCl(COT) complex.

A structure determination of the 1 : 1 adduct of norbornadiene with copper(I) chloride revealed a cyclic tetrameric structure with $\bar{4}$ symmetry [274]. The copper and chlorine atoms alternate in an eight-membered, tub-shaped Cu_4Cl_4 ring (Cu—Cl = 2.296, 2.275 Å). One olefinic linkage of the diene is coordinated and completes a distorted trigonal coordination at copper (Cu—C = 2.051, 2.111 Å). Angles at copper range from 104.4 to 130.9°, similar to that found in $[CuCl(COT)]_n$. The closest axial contact is 3.091 Å to a chlorine atom. The structure of $[CuCl(norb)]_4$ is closely related to that of CuCl(2-butyne) [275]. The latter compound also contains a Cu_4Cl_4 ring with $\bar{4}$ symmetry with the acetylenic group lying in a $CuCl_2$ plane. However, the $CuCl_2$(COD) complex (COD = 1,5-cyclo-octadiene) is dimeric; both olefinic linkages are bonded and the chloride bridges produce a pseudotetrahedral structure around copper [276].

The structure of the complex Cu_2Cl_2 (*trans*-cyclo-octene)$_3$ is dinuclear with two chlorides bridging the two copper atoms. One copper is bonded to two bridging chlorides plus two olefin ligands; thus, it has a distorted tetrahedral geometry. The second copper atom bonds to the two bridging chlorides and one olefin which lies in the $CuCl_2$ plane; it has a distorted trigonal-planar geometry (angles at Cu are 102, 128, 129°) [277].

Bruce and co-workers [278,279] recently found that reactions between $[RuCl(PPh_3)_2(C_5H_5)]$ and substituted copper(I) arylacetylides ($Cu(C_2R)$, R = C_6H_4-*p*-CH_3, and C_6H_4-*p*-F), produced the rather unusual three-coordinate copper(I) complex (BB) [278]. On the basis of the X-ray structure determination of $[ReCu(C_2C_6F_5)_2(CO)_3PPh_3]$ (CC), the $[RuCu(C_2C_6H_4\text{-}p\text{-}CH_3)_2PPh_3\text{-}(C_5H_5)]$ complex is formulated as a zwitterion aggregate of $[Cu(PPh_3)]^+$ and $[Ru(C_2Ar)_2(C_5H_5)]^-$ in which the copper atom is π-bonded to both acetylene groups. Similarly, treatment of $Cu(C_2C_6F_5)$ with *cis*-$[ReCl(CO)_3(PPh_3)_2]$ produced $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$ in 21% yield as one of three products. Structure (CC) was proven by X-ray crystallography [279], and the copper atom is trigonally bonded to one phosphorus atom and two C≡C linkages. Neither of the Ru—Cu and Re—Cu complexes have any metal—metal bonding, and the metals attain the 18-electron configuration formulated as Ru(II) Cu(I) and Re(I)—Cu(I), respectively.

Copper(I) halides are reported to react with 1,4-diazabuta-1,3-dienes to form strongly colored 1 : 1 adducts [280]. Three-coordinate monomeric structures were assigned on the basis of infrared and visible spectroscopy.

(g) Miscellaneous examples of three-coordinate complexes

In this section we shall discuss several three-coordinate complexes of Group IB, Group IIB, and transition metals in which the donor ligands do not fit the major categories discussed earlier. Additionally, selected three-coordinate complexes containing main group metals will be discussed. Finally, we present two examples of the many sulfide minerals that contain three-coordinate metal atoms.

(i) Group IB, Group IIB, and transition metal complexes

Aromatic amines from a series of three-coordinate complexes, $[CuL_3]$-ClO_4), where L = 2-picoline, 2,5-lutidine, 2-ethylpyridine, and 2-isopropylpyridine [281]. The 2-picoline complex has a nearly planar CuL_3 core (Fig. 33) with Cu—N distances of 1.97, 1.98, and 2.02 Å, and N—Cu—N angles of 113, 118, and 139°. The steric requirements of the *o*-methyl groups force two phenyl groups to be nearly orthogonal and one phenyl group to be nearly coplanar with the CuN_3 plane. Steric interactions probably also cause the observed deviations from trigonal-planar symmetry around copper.

The diphenylazide ion forms a 1 : 1 dinuclear copper(I) complex whose structure somewhat resembles that of copper(II) acetate. The N—Cu—N angle is 171.8° [282]. The geometry at copper would be described as essentially linear except for the extremely short Cu—Cu distance (2.45 Å).

Canty et al. [123] have shown that bipyridyl, phenanthroline, and derivatives of these ligands form 1 : 1 complexes with methyl mercury(II) nitrate. NMR spectroscopy indicated three-coordinate $Hg(CH_3)L$ cations, which was confirmed by a structure determination of the 2,2′-bipyridyl salt (Fig. 34).

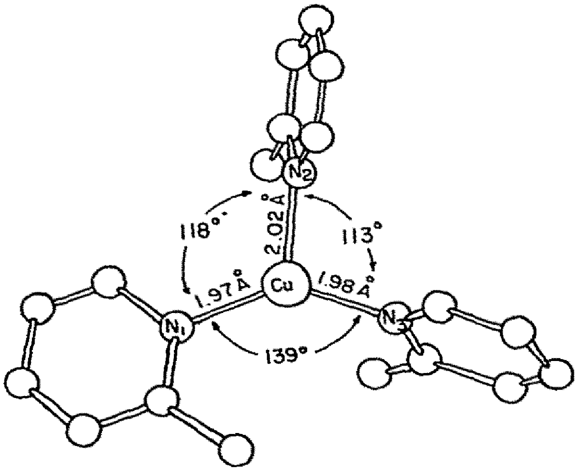


Fig. 33. A drawing of the cation $[Cu(2\text{-picoline})_3]^+$. Reproduced with permission from ref. 281.

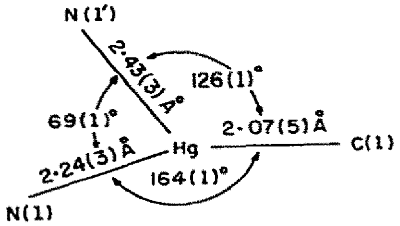


Fig. 34. Stereochemistry around mercury in $[(CH_3)Hg(2,2'\text{-bipy})]NO_3$. Adapted with permission from ref. 123.

The coordination geometry is planar but distorted markedly from trigonal symmetry toward the more common linear coordination of mercury. The Hg—N distances are 2.24(4) and 2.42(3) Å, and the C—Hg—N angles are 164(2) and 126(2)°.

The complex [Cu(en)(CO)]Cl has been obtained from the reaction of Cu(CO)Cl with ethylenediamine in methanol at —30°C [283]. Conductivity and infrared measurements indicate the presence of three-coordinate $[Cu(en)(CO)]^+$ cations in methanol solution and in the solid state. A similar preparation at —20°C gave a different compound that appears to contain dinuclear, carbonyl-bridged $[(en)Cu(CO)_2Cu(en)]^{2+}$ cations, which apparently dissociate to monomeric ions.

Copper—thiolate compounds of several different compositions and structures can be formed under different preparative conditions. Recently, interesting trigonal-planar Cu(I) coordination geometries were found in the clusters, $[Cu_5(SBu^t)_6]^-$ [284], $[Cu_4(SPh)_6]^{2-}$ [223], and $[Cu(I)_8Cu(II)_6L_{12}Cl]^{5-}$ ($L = SC(Me_2)CH(NH_2)CO_2^-$) [285]. The $[Cu_5(SBu^t)_6]^-$ cluster has five copper atoms arrayed as a regular trigonal bipyramid, $Cu_{ax}—Cu_{eq}$ = 2.72 ± 0.01 Å, and $Cu_{eq}—Cu_{eq}$ = 3.23 ± 0.04 Å (Fig. 35). Each of the six sulfur atoms bridges an axial—equatorial pair of copper atoms so that the two axial copper atoms are trigonal-planar and the three equatorial copper atoms have approximately linear coordination. The structure of $[Cu_4(SPh)_6]^{2-}$ contains a Cu_4S_6 core [223] very similar to that reported recently for the $[Cu_4(\text{thiourea})_6]^{4+}$ cation [194]. The six SPh^- ligands bridge the edges of the Cu_4 tetrahedron, and the coordination around each copper is distorted trigonal and nearly planar (Fig. 36). The Cu—S bond lengths vary over the range 2.24(1) to 2.34(1) Å with an average value of 2.29 Å. The S—Cu—S angles vary from 101(1) to 138(1)°, the average value being 120°.

The structure of the intensely purple complex formed by copper(II) and D-penicillamine (L) consists of the mixed-valence clusters $[Cu(I)_8Cu(II)_6L_{12}Cl]^{5-}$ [285]. Eight of the copper(I) atoms are each surrounded by three penicillamine S(thiol) atoms in an approximately trigonal-planar geometry. Six copper(II) atoms are each bonded to the N(amino) and S(thiol) atoms of two *cis* chelating penicillamine ligands. Every thiol sulfur atom in the structure is thus bonded to one Cu(II) and two Cu(I) atoms.

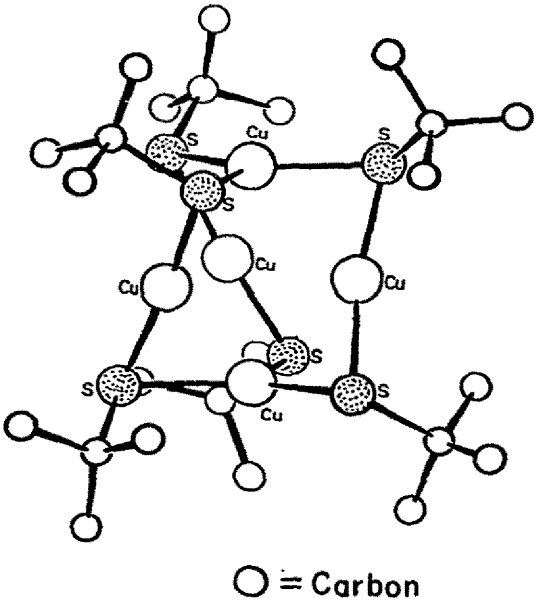


Fig. 35. A drawing of the [$Cu_5(SBu^t)_6]^-$ cluster. The copper atoms at the top and bottom sites of the Cu_5 unit are trigonal planar. Reproduced with permission from ref. 284.

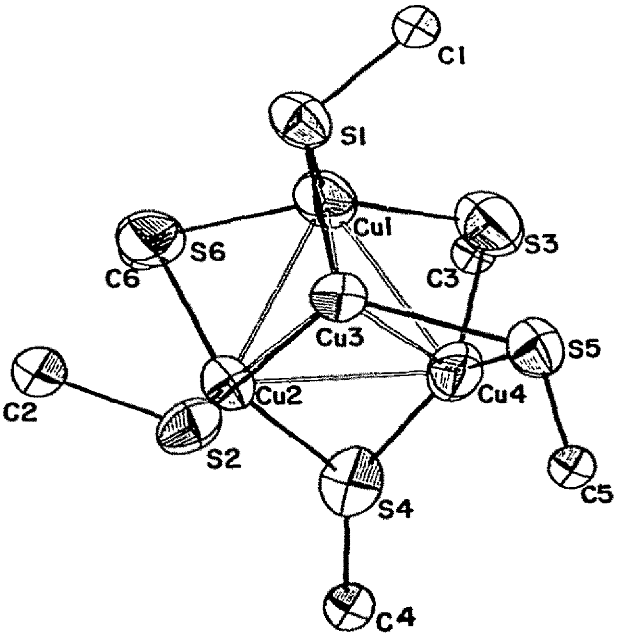
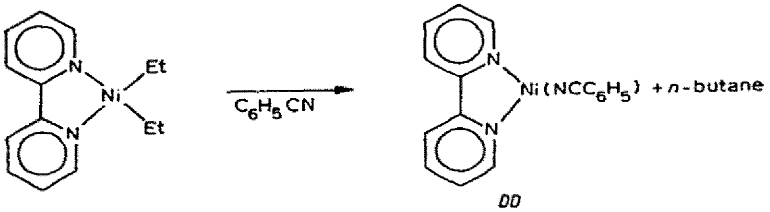


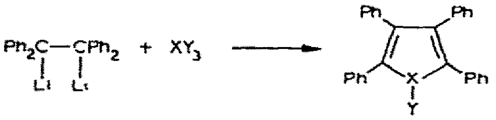
Fig. 36. Structure and labeling of the anion $[Cu_4(SPh)_6]^{2-}$. Only the carbons attached to the respective sulfur atoms are shown. The remaining carbon atoms of the phenyl rings have been omitted for clarity. Reproduced with permission from ref. 223.

Uchino and Ikeda [286] prepared a nickel(0) compound (DD), which is an extremely active polymerization catalyst for acrylonitrile, by the reaction given in eqn. 40. Although the structure of (DD) has not been determined by X-ray crystallography, it is formulated as a three-coordinate nickel(0) complex on the basis of its sharp infrared absorption of 2105 cm^{-1}, which is ~150 cm^{-1} lower than that of free benzonitrile.



(40)

Treatment of tetraphenyldilithioethane with XY_3 compounds (X = Au, Hg, B, Tl) produces heterocyclic compounds that incorporate the metal atom into three-coordinate sites (eqn. 41) [287].



(41)

(ii) Selected main-group metal complexes

Crystal structures have been reported for several three-coordinate complexes that contain metal—metal bonds. The compound $Tl[Mo(CO)_3(\pi\text{-}C_5H_5)]_3$ has a pyramidal structure with the three $Mo(CO)_3(\pi\text{-}C_5H_5)^-$ groups disposed almost symetrically about the central thallium atom [288]. The thallium atom lies 0.586 Å out of the plane of the three attached molybdenum atoms, the Tl—Mo distances range from 2.938 to 3.001 Å, and the Mo—Tl—Mo angles range from 113.92 to 122.66°. Other similar TlL_3 compounds have been synthesized [L = $Mn(CO)_5$, $SiMe_3$, $Co(CO)_4$], and they presumably have analogous structures [289,290].

A number of compounds of the type $XGaL_2$, X_2GaL, InL_3, $XInL_2$, and X_2InL (X = Cl or Br and L = $Mn(CO)_5$ or $Co(CO)_4$) have been reported [291, 292]. One of these compounds, $In[Co(CO)_4]_3$, is known to consist of discrete molecules in which each indium atom is surrounded by three $Co(CO)_4^-$ groups in a trigonal-planar arrangement (Fig. 37) [293]. The indium atom lies within 0.009 Å of the Co_3 plane, the In—Co distances are 2.590 to 2.597 Å, and the Co—In—Co angles are 119.31 to 120.88°. The closest intermolecular contact to indium involves an oxygen at 3.71 Å. The structure resembles that of $In(CH_3)_3$, which contains trigonal-planar molecular units in a loose tetrameric array with very weak axial contacts (3.10 Å) to carbon atoms of an adjacent $In(CH_3)_3$ molecule [294]. The InR_3 compounds with larger R groups also appear to be monomeric. The structure of $Tl(CH_3)_3$ is

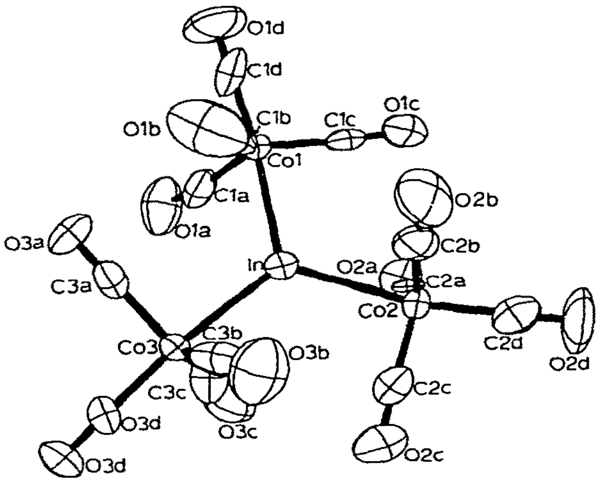


Fig. 37. Molecular structure of In[Co(CO)$_4$]$_3$. The geometry around indium is trigonal planar with an average In—Co bond distance of 2.594(3) Å. Reproduced with permission from ref. 293.

similar [295] to that of In(CH$_3$)$_3$, except that the interaction with the adjacent unit is much stronger and the coordination geometry is best described as a distorted trigonal bipyramid.

Indium has a trigonal-planar coordination geometry in InPh$_3$, with additional weak interactions to phenyl rings in adjacent InPh$_3$ molecules (In—C = 3.1 Å) [295]. The analogous gallium compound, GaPh$_3$, has a similar structure, but the axial Ga—C separations (3.42 Å) are essentially non-bonding in this case.

Crystal structure studies confirm a dimeric structure for Al(CH$_3$)$_3$ [297]. Early vapor pressure studies by Laubengayer and Gilliam [298] showed that Al(CH$_3$)$_3$ exists as a dimer in the vapor state up to 70° C, AlEt$_3$ is 12% dimerized at 150° C, and GaEt$_3$ and InMe$_3$ are monomeric in the vapor state and in cyclopentane [299].

The nominally three-coordinate lanthanide complex Er[Co(CO)$_4$]$_3$ · 4THF was obtained [300] from the reaction of bis(tetracarbonylcobalt)mercury with an Er—Hg amalgam in THF. The compound is a dark-red, air- and water-sensitive solid that was characterized by infrared and mass spectral methods; however, there is a high probability that some THF molecules are coordinated.

(iii) Minerals

Despite the fact that widespread recognition of the existence of three coordination in metal complexes is relatively recent, any review of three coordination would be incomplete without pointing out that three coordination occurs in numerous well-known mineral structures (especially among the copper sulfide minerals). We shall limit our discussion to only a few common and illustrative examples.

The hexagonal mineral covellite, CuS, illustrates how seemingly simple binary formulations sometimes conceal much more complex (and much more interesting) structures [301]. The lattice contains two thirds of the sulfur as disulfide units (S_2, as in pyrites) and one third of the copper atoms in a trigonal-planar environment (Cu—S = 2.32 Å). Hence, the formulation of covellite might be considered $Cu(I)_4\ Cu(II)_2\ (S_2)_2S_2$.

Digenite, Cu_9S_5, is another binary copper sulfide mineral that contains copper in a variety of coordination environments. Per formula unit, digenite has two trigonal-planar copper atoms (Cu—S = 2.26 Å), as well as two distorted tetrahedral, four regular tetrahedral, and one octahedral copper atom [302]. The mineral is best formulated as $Cu(I)_8Cu(II)S_5$.

Bornite (Cu_5FeS_4) and stromeyerite (AgCuS) are other minerals containing trigonal-planar copper bound to sulfur [303]. Further description of these and other sulfide minerals that contain three-coordinate metal atoms may be found in Wells' compilation [304].

Seff and co-workers have shown [305] that certain Mn(II)-exchanged zeolites contain trigonal-bipyramidal Mn(II) ions, which become trigonal planar on dehydration. Sodium ions also become three-coordinate in the dehydrated material. An interesting review by Kellerman and Klier [306] on intrazeolitic transition metal complexes deals with the ligand field aspects of transition metal ions occupying trigonal sites in synthetic zeolites.

IV. SUMMARY

This review has brought into focus a rich variety of three-coordinate compounds covering a wide range of elements, valence states, and ligand types. The formal oxidation states of —I, 0, I, II, and III are exhibited with "soft" ligands stabilizing the lower oxidation states and "hard" ligands favoring the higher oxidation states. Steric hindrance plays a major role in limiting the coordination number to three for elements which normally favor a higher coordination number. Thus even the lanthanides, which normally adopt rather high coordination numbers, may be constrained to three coordination by using sufficiently bulky ligands.

In some cases a delicate balance is struck between opposing steric and electronic factors, resulting in solution equilibria due to the accessibility of more than one coordination number. Such systems are often noteworthy for their involvement in catalytic processes. Perhaps the most striking feature to emerge from this survey is the fact that the geometry of three-coordination is by no means confined to a trigonal-planar configuration (D_{3h} local symmetry) since examples of pyramidal (C_{3v}) and lower (C_{2v}) symmetry are found. In this context some recent theoretical studies have proved to be very illuminating in exploring the electronic aspects of the symmetry of three-coordination. Tolman's development of the "cone-angle" concept of the steric effect of axially symmetric ligands has provided valuable insight into factors favoring low coordination number, but more theoretical work is required for bulky ligands of lower symmetry.

In Section II dealing with "hard" ligands it is noteworthy that three-coordinate examples are found for all of the 3*d*-transition elements, covering oxidation states (I), (II), and (III) and *d*-electron configurations of d^1, d^2, d^3, d^5, d^7, d^8, d^9, and d^{10}. There seems to be no inherent reason preventing the stabilization of examples with d^4 or d^6 configurations and further synthetic work may remedy these deficiencies. Also, it should be possible to obtain three-coordinate compounds of 4*d*and 5*d* transition metals and the actinides.

Section II is mainly concerned with spectroscopic and structural aspects of the three-coordinate transition metals. The results show that substantial ligand field stabilization may be present although it is by no means a prerequisite for obtaining a stable three-coordinate complex. In fact the steric effect of the ligand must be the major controlling factor in this field. This view is supported by the existence of three-coordinate Si(III), Ge(III), and Sn(III) compounds involving bulky ligands.

Section III deals with "soft" ligands; here it is noteworthy that three-coordination is dominated by the d^{10} metal species; Ni(0), Pd(0), Pt(0), Cu(I), Ag(I), Au(I) and Hg(II), in conjunction with a wide range of ligands such as sulfur- or phosphorus-donors, halides, pseudo-halides, carbon monoxide, dinitrogen, olefins, etc. This section also deals with the catalytic behavior of these compounds together with three-coordinate compounds of Ru(II)(d^6) and Rh(I)(d^8). Although steric factors undoubtedly play an important part in stabilizing these complexes it is clear that electronic factors are also of considerable importance. Thus most of these compounds involve π-acceptor ligands with low valent d^{10} metals.

In conclusion, we contend that three-coordination is not just an academic curiosity but is fairly widespread and of considerable academic and practical significance. This review suggests that the chemistry of three-coordination has many interesting problems still to be solved. It is an active field and new developments may be expected.

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